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Hyperfine Fields at ^{55}Mn in Ordered Au-Mn Alloys from Low-Temperature Specific-Heat Measurements

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The specific heat of the ordered alloys AuMn, Au_2Mn, Au_3Mn, Au_4Mn, and $AuMn_3$ has been measured in the temperature range from 0.25 to 3.9 °K. In addition to the electronic, lattice, and nuclear Schottky contributions to the total specific heat, the results show an anomaly at temperatures below about 0.6 °K, the origin of which may be associated with magnetic ordering. The variation with composition of the hyperfine field is discussed in terms of the magnetic environment of the ^{55}Mn nucleus.

I. INTRODUCTION

The hyperfine field at the host nuclei in binary alloys of transition metals with nonmagnetic impurities is known to depend markedly on the magnetic environment. For this reason the study of hyperfine coupling in ordered alloys is very useful, because the magnetic environment of the host nuclei should be well defined. Alloys of manganese and gold form a suitable system for study by the specific-heat method, since five ordered phases, AuMn, Au_2Mn, Au_3Mn, Au_4Mn, and $AuMn_3$ are formed. Since the gold nuclei carry a magnetic moment of 0.144 86 μ_N, the total nuclear specific heat must be corrected for the contribution from the gold hyperfine interaction. Fortunately, ^{197}Au has a resonance γ ray suitable for Mössbauer effect measurements, thus enabling this correction to be made.

The hyperfine field at the ^{55}Mn nuclei in these five ordered Au-Mn alloys has been deduced from the results of specific-heat measurements made in the temperature range from 0.25 to 3.9 °K. The specific-heat results were corrected using the values of the hyperfine field at the gold nuclei as obtained by Patterson *et al.*[1] from Mössbauer measurements on samples from the same melts.

In addition to the T^{-2} contribution to the specific heat, arising from the nuclear hyperfine interaction, a further positive contribution was observed, and is discussed in a later section.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Details of the preparation of the specimens and the annealing procedures for producing the ordered phases, together with the results of an x-ray analysis, are given by Patterson *et al.*[1] The specific-heat measurements were made initially in the temperature range from 0.25 to 1 °K, with an adiabatic demagnetization cryostat, but this range was later extended up to 3.9 °K by the use of a ^{3}He cryostat, which has been described elsewhere.[2] The results are plotted as specific heat C against temperature T in Fig. 1. There is good agreement between the two sets of results in the overlapping temperature region.

At temperatures below 4 °K the total specific heat of a normal ferro- or antiferromagnet can usually be represented by the equation

$$C=\gamma T+AT^3+BT^{-2}, \qquad (1)$$

where γ and A are the coefficients of the electronic and lattice specific-heat contributions, respectively, and B is the coefficient of the first term in the expansion of the nuclear Schottky specific heat. Spin-wave contributions have been omitted from the above expression because they are expected to be small and are difficult to separate from the lattice contribution in measurements below 4 °K. If the lattice contribution is subtracted from the total specific heat, and the remainder is plotted as CT^2 against T^3, a straight line should result.

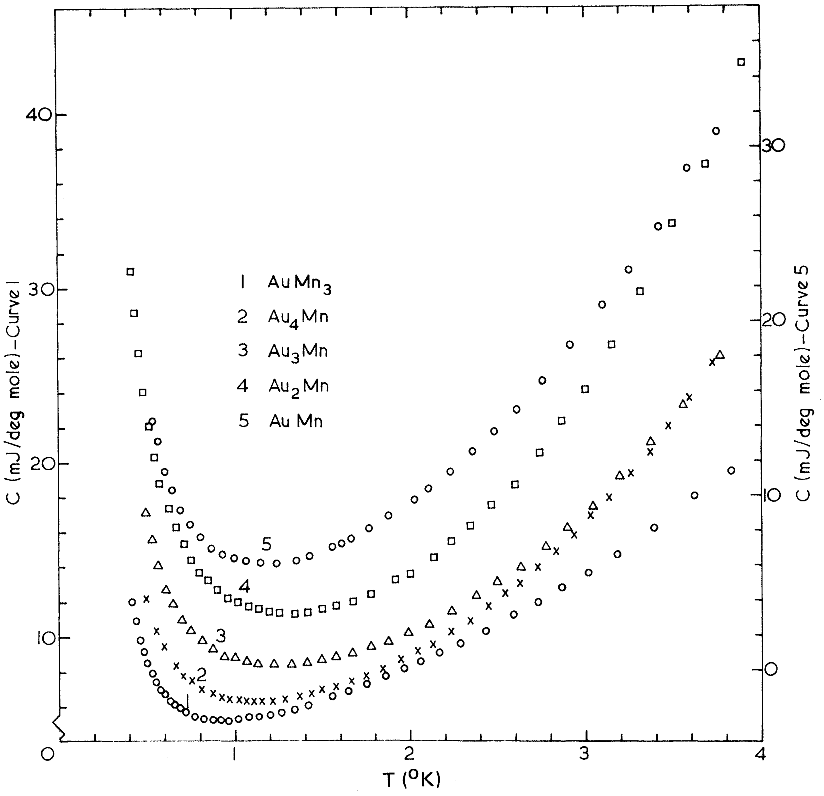

FIG. 1. Specific heat as a function of temperature for ordered Au-Mn alloys, obtained from measurements with the ^{3}He cryostat. The left-hand ordinate scale corresponds to curve 1, for AuMn$_3$. To avoid overlap, the ordinate scale for each successive curve is shifted up by 2 mJ/deg mole with respect to that for the previous curve. The right-hand ordinate scale therefore corresponds to curve 5, for AuMn.

However, it can be seen from Fig. 2 that when the present results below 1 °K for each alloy are plotted in this form there is a positive deviation from the expected straight line at temperatures below about 0.6 °K. Consequently, the experimental points below this temperature have been omitted from the least-squares analyses, which fitted the data to Eq. (1). The specific-heat parameters obtained in this way are given in Table I. The errors quoted arise from the scatter in the experimental points and from the uncertainty in the extent of the positive deviation at the lower temperatures. Also included in the table are the values of H_{eff} at the ^{197}Au nuclei, obtained from the Mössbauer measurements, and the values of H_{eff} at the ^{55}Mn nuclei, deduced from the specific-heat coefficient B after correction for the contribution from the gold hyperfine interaction.

III. DISCUSSION

A. Electronic Specific-Heat Coefficient γ

The variation of the specific-heat parameter γ with manganese concentration for the ordered Au-Mn alloys is shown in Fig. 3. It can be seen that γ decreases with increasing manganese concentration to a minimum at about 35% Mn, after which it increases. Since the electronic specific-heat coefficient of γ-Mn is 9.2 mJ/deg^2 mole,[3] γ must obviously increase very rapidly at some point after the concentration corresponding to AuMn$_3$. At the gold-rich end of the alloy system, the value of γ for dilute Mn in Au is 8.5 mJ/deg^2 mole[4] compared with the value of 0.69 mJ/deg^2 mole for pure gold.[5] This large difference may arise from a magnetic contribution to the specific heat, since the addition of a fraction of a per cent of manganese to gold is unlikely to cause such a large change in the density of states at the Fermi surface.

It seems likely therefore that the electronic coefficient for the dilute alloys of Mn in Au is close to the value for pure gold. The additional contribution to γ, observed by du Chatenier and Miedema,[4] is independent of concentration, and can be explained by a magnetic contribution of the type proposed by Marshall,[6] where a small number of spins sit in regions of near-zero field. In the case of the ordered alloys, a similar situation could arise from incomplete ordering. These alloys may therefore also have a specific-heat contribution which is of magnetic origin. This question could be resolved by making measurements after cooling the specimens in a magnetic field, as the magnetic con-

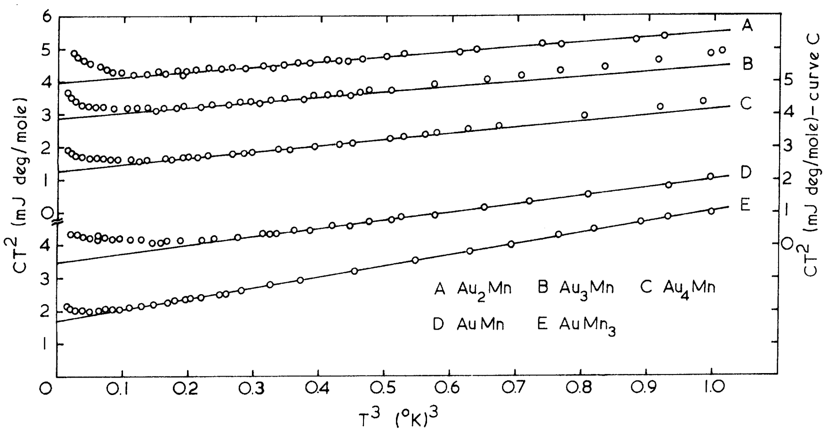

FIG. 2. CT^2 against T^3 for the data below 1 °K. To avoid overlap, the lower left-hand ordinate scale corresponds to curves D and E, while the upper scale corresponds to curves A and B. The right-hand ordinate scale corresponds to curve C.

tribution should then change.

B. Hyperfine Field H_{eff}

The hyperfine field at the ^{55}Mn nuclei is shown as a function of manganese concentration for the gold-manganese system in Fig. 3. A value of H_{eff} for dilute Mn in Au is not included in the figure because of lack of agreement in the published results. The specific-heat measurements of du Chatenier and Miedema[4] yield a value for H_{eff} of 340 kOe, while the value obtained from nuclear orientation measurements by Cameron *et al.*[7] is 400 kOe. The reason for this discrepancy is not understood, since a value derived from specific-heat measurements without correction for a field at the gold nuclei would increase the difference between the two values. The higher value appears to be more compatible with the present results which indicate an almost constant effective field for manganese concentrations up to 34%. As the Mn concentration is further increased, H_{eff} decreases almost linearly from 422 kOe at 34% Mn to 57 kOe for γ-Mn.

The present value for the equiatomic alloy AuMn, which has a body-centered tetragonal crystal structure with a c/a ratio greater than 1, is 334 kOe, compared with the value of 320 kOe obtained by Ho and Bindloss[8] for an alloy of slightly higher gold concentration, for which c/a is less than 1. This latter value was derived from specific-heat measurements below 1 °K, but the lattice contribution was not taken into account. The effect of neglecting this term for the Au-Mn alloys below 1 °K is illustrated in Fig. 2 in the cases of Au_3Mn and Au_4Mn. Such an interpretation of the data leads to values of γ and B which are higher and lower, respectively, than the corrected values.

An attempt can be made to correlate the effective field at the host nucleus with the number, magnitude, and direction of the magnetic moments on the nearest-neighbor atoms. This semiempirical approach yields an equation of the form

$$H_{eff} = a\mu_{host} + b\mu_{host}\bar{\mu}_{nn} \quad , \tag{2}$$

where a and b are constants, μ_{host} is the magnetic moment of the host atom, and $\bar{\mu}_{nn}$ is the mean moment of the nearest-neighbor atoms. This equation has been used with reasonable success by Proctor *et al.*[9] and Streever[10] for the Ni-Mn alloy system.

For the Au-Mn system, the value of a can be estimated from the data on dilute alloys of Mn in Au, where the manganese atoms carry a moment of 5β, and H_{eff} at the ^{55}Mn nuclei is assumed to be -400 kOe. Since the mean magnetic moment of the nearest magnetic neighbors is zero, the constant a is -80 kOe/β. Using this value of a, the second constant b can be derived from the data on Au_2Mn. In this alloy, each manganese atom has eight nearest-neighbor and two next-nearest-neighbor gold atoms, all having zero magnetic moment, and four third-nearest-neighbor manganese atoms. The latter, which have a moment of 3.6β,[11] are the nearest magnetic neighbors. As they are in ferromagnetic alignment with the host atom, the mean moment is $+1.03\beta$. Since H_{eff} is 422 kOe, assumed to be negative also, the constant b takes the value -36 kOe/β^2.

In the equiatomic alloy AuMn, each manganese atom has eight gold nearest neighbors, whose moment is zero, and four next-nearest-neighbor manganese atoms, of which two are ferromagnetically and two are antiferromagnetically aligned with the host atom. The mean moment of the neighbor environment is therefore zero. Using the values for the constants derived above, the value of H_{eff} predicted from Eq. (2) is -336 kOe, which is in good agreement with the present experimental value of -334 kOe.

It is not possible to extend the correlation to the ordered Au_3Mn, Au_4Mn, and $AuMn_3$ alloys, because although the crystal structures are known, the magnetic structure has not been determined by

TABLE I. Specific-heat parameters and hyperfine fields at ^{197}Au and ^{55}Mn nuclei for the Au-Mn alloy system.

	at.% Mn	γ (mJ/deg^2 mole)	A (mJ/deg^4 mole)	B (mJ deg/mole)	H_{Au} (kOe)	H_{Mn} (kOe)
$AuMn_3$	75.24	3.35 ± 0.06	0.11 ± 0.01	1.69 ± 0.11	272	190 ± 6
AuMn	50.00	2.79 ± 0.08	0.39 ± 0.01	3.47 ± 0.05	0	334 ± 3
Au_2Mn	33.94	1.53 ± 0.11	0.55 ± 0.01	3.96 ± 0.04	1570	422 ± 4
Au_3Mn	24.82	1.60 ± 0.08	0.29 ± 0.01	2.86 ± 0.04	780	425 ± 4
Au_4Mn	19.63	1.89 ± 0.07	0.31 ± 0.01	2.24 ± 0.04	~700	423 ± 4

neutron diffraction measurements. However, the change in H_{eff} with manganese concentration can be understood qualitatively.

In the dilute alloys, where the field is about −400 kOe, each manganese atom has on average only gold nearest neighbors, and H_{eff} arises from the first term of Eq. (2). As the manganese concentration is increased to the composition Au_2Mn, the environment of the host manganese atom changes very little, although some of the higher-order gold neighbors have been replaced by manganese atoms. Any change in H_{eff} would then be expected to be small. For AuMn, the second- and third-nearest neighbors are all manganese atoms, and for $AuMn_3$ the nearest-neighbor atoms are manganese, while the gold atoms now occupy higher-order neighbor sites. The antiferromagnetic exchange interaction between the host and the neighbors contributes a positive term to the hyperfine field, causing the observed reduction in the negative field. Finally, in γ-manganese antiferromagnetically aligned nearest-neighbor manganese atoms are more numerous, and closer to the host atoms, than in any of the alloys. The hyperfine field is therefore lowest, as is observed experimentally.

C. Anomalous Specific Heat

The positive deviation from a straight line in the plot of CT^2 against T^3 for all the Au-Mn alloys does not appear to be explainable in terms of conventional magnetic dipole and electric quadrupole interactions for the reasons given below.

In the presence of a large magnetic hyperfine interaction, the description of the nuclear specific heat by a T^{-2} coefficient may be incomplete, and a further term proportional to T^{-4} must be included. This additional term would cause a negative deviation from the straight-line plot of CT^2 against T^3.

In addition to the magnetic hyperfine interaction, the nuclei may experience a quadrupole interaction arising from an electric field gradient (efg) at the nucleus. If the hyperfine field is parallel to the efg the coefficients of the nuclear specific heat will be modified by this interaction, and a further term proportional to T^{-3} must be included. Even if this contribution were large, which is unlikely in view of the experimental evidence for other alloys with manganese, the coefficients of the T^{-3} and T^{-4} terms are negative,[12] which would again cause a negative deviation.

In the case of Au_2Mn, the Mössbauer measurements show that the efg at the gold nucleus is perpendicular to the magnetic field. If this condition applied to the Mn nuclei, then our calculations have shown that this would give rise to a positive coefficient of the T^{-3} specific-heat term. If the quadrupole splitting were large enough, this positive coefficient could become larger than the negative coefficient of the T^{-4} term, leading to a positive deviation.

The present results for all the alloys show that the anomalous specific heat increases with decreasing temperature at a much faster rate than would a positive T^{-3} contribution. A quadrupole interaction occurring when the efg and the magnetic field are at right angles does not therefore appear to provide an explanation of the anomaly.

The anomaly could be the result of a calorimetric error, but is not believed to be so for several reasons. Although the deviation is a characteristic sign of deterioration of the thermometer, a Speer 470-Ω ½-W resistor, the same effect was observed on repeating the measurements with a new Speer thermometer. Further, among all the specimens which have been measured in the adiabatic demagnetization cryostat, only the gold-manganese alloys show the anomaly; also, the results of measurements made on a specimen of chromium immediately afterwards with the same thermometer reflected only the usual behavior of an antiferromagnet. In addition, the results are in good agreement with those obtained from measurements with the ^{3}He cryostat using similar Speer resistors.

Therefore, in order to explain the anomaly in this way there must be a fundamental error in the calorimetric technique used in this laboratory. This possibility can be ruled out because previous measurements using the ^{3}He cryostat have yielded completely normal data giving a value of H_{eff} at ^{55}Mn in a disordered alloy of Ni_3Mn [9] in good agreement with the recent NMR results of Streever.[10]

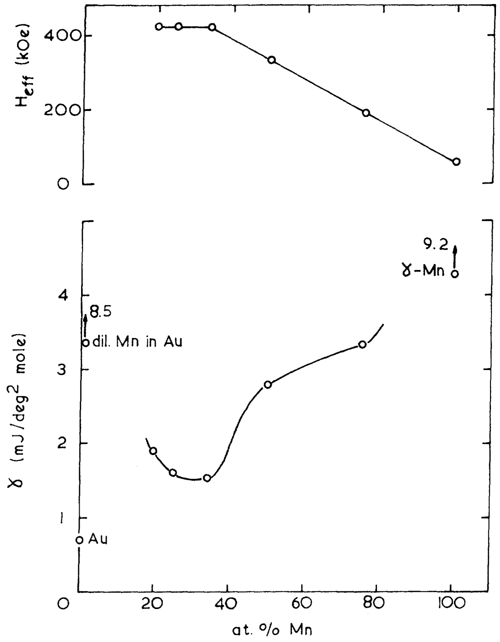

FIG. 3. Specific-heat parameter γ and hyperfine field at the ^{55}Mn nuclei plotted as a function of Mn concentration for the Au-Mn alloy system.

Both cryostats have also yielded a value of H_{eff} at ^{59}Co in hcp cobalt[13,14] in good agreement with the value currently accepted as a standard NMR result.

In view of these findings we believe that the anomaly is a genuine physical effect, probably having its origin in some type of magnetic ordering. This idea is strengthened by our previous work on Ni_3Mn,[9] which exhibits the start of a similar anomaly in approximately the same temperature range but only when the alloy is partially or completely ordered. The results for the disordered alloy show no unusual behavior. The anomaly could therefore be associated with some form of magnetic ordering, produced by incomplete ordering of the crystal structure.

For the Au-Mn system, the x-ray analyses indicate that small amounts of impurity phases are present in each alloy, except in Au_4Mn. However, for this latter alloy, the Mössbauer results are indicative of an impurity phase not detected by the x-ray analysis. The magnetic ordering might therefore arise from the presence of these impurity phases.

The anomalous specific heat was not observed by Ho and Bindloss[8] in their results below 1 °K on the equiatomic alloy AuMn. They obtained a value for γ of 1.05 mJ/deg^2 mole, compared with our value of 2.79 mJ/deg^2 mole, although the values of H_{eff} are in reasonable agreement. Also, instead of a positive deviation from the plot of CT^2 against T^3, they observed a negative deviation with a T^{-4} dependence starting at much lower temperatures, which was attributed to the second term in the expansion of the nuclear Schottky anomaly. The two sets of results are not necessarily in conflict, because the specimen used by Ho and Bindloss was cut from a twinned single crystal of slightly higher gold concentration, for which the c/a ratio is less than 1. The difference in magnetic structure arising from the difference in composition of the two specimens may therefore be responsible.

IV. CONCLUSIONS

The results of specific-heat measurements made on five ordered alloys of gold and manganese indicate that the contribution which is linear in temperature may contain a magnetic component.

The hyperfine field at the ^{55}Mn nucleus can be correlated qualitatively with the surrounding magnetic environment. The quantitative discussion of H_{eff} is limited to the alloys AuMn, Au_2Mn, and dilute Mn in Au, because of the lack of detailed knowledge of the magnetic structure of the other alloys. Nevertheless, the constants of Eq. (2) derived for this alloy system are not widely different from those obtained previously for the Ni-Mn system.

In addition to the lattice, electronic, and nuclear specific-heat contributions, an anomalous contribution was observed for all the alloys at temperatures below about 0.6 °K. Because the anomaly cannot be explained in terms of conventional magnetic dipole and electric quadrupole interactions or attributed to a calorimetric error, the existence of a specific-heat contribution associated with some form of magnetic ordering is postulated.

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Expansion Theorems for Magnetic-Resonance Line Shapes

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We have found an exact expression or expansion theorem for a free-induction-decay (FID) curve which involves all the moments of the corresponding cw absorption line as well as two arbitrary scale factors or parameters which may be chosen to optimize the convergence which is necessarily uniform. The expression obtained is a generalization of Taylor's theorem known as a Newmann expansion, and it gives an FID curve as either an exponential or Gaussian damping factor times an infinite series of Bessel functions which may describe the oscillations characteristic of certain FID shapes. Any one of the (infinitely) many Bessel-function expansions may be used to represent a particular FID curve, although there will be one which requires the fewest terms for a specified accuracy of approximation. Application of these expansions to FID curves from calcium fluoride shows that it is possible to obtain an excellent fit to the data, using only the theoretical second and fourth moments for the expansion whose leading term corresponds to Abragam's trial function. Furthermore, when several exact but different expansions were truncated to only three terms it was found that they were nearly equal to each other and to the data over a major portion of the decay for the optimum choice of the two scale factors. Another application of these expansions would be the determination of the moments of a given FID curve, using the orthogonality integral for Bessel functions.

I. INTRODUCTION

The problem of calculating the shape of magnetic resonance absorption lines was first discussed by Van Vleck[1] who showed that the moments of the line could be calculated exactly. The $2n$th moment of a normalized line-shape function $G(\omega)$ is given by

$$M_{2n}=\int_0^\infty \omega^{2n}G(\omega)\,d\omega,$$

where

$$\int_0^\infty G(\omega)\,d\omega=1$$

and $\omega=0$ corresponds to the center of the line. Since $G(\omega)$ is symmetric about its center, the odd moments are zero. The second and fourth moments were evaluated by Van Vleck[1] for a system of spins on a lattice with dipole-dipole and exchange interactions and were found to agree with experimental measurements on calcium fluoride.[2,3] An important result of these calculations was that a quantitative theoretical test was provided to determine the degree of Gaussian or Lorentzian character of an absorption line, these shapes being characteristic of magnetic resonance lines in general.[2,4] Thus, for example, the resonance line shape(s) from calcium fluoride could be shown to deviate somewhat from the Gaussian shape predicted by the local-field model of Bloembergen, Purcell, and Pound.[4]

Further development in the theory was made by Lowe and Norberg[5] who showed that a line-shape function $G(\omega)$ was the Fourier transform of the corresponding free-induction-decay (FID) function $F(t)$ which represents the amplitude of the magnetization following a 90° rf pulse. Consequently,

$$F(t)=\int_0^\infty \cos(\omega t)\,G(\omega)\,d\omega,$$

and, therefore,

$$F(t)=\sum_{n=0}^{\infty}(-1)^n M_{2n}\frac{t^{2n}}{(2n)!}\ . \tag{1}$$

This expansion theorem gives an exact expression for the line shape in terms of Van Vleck's moments, although many terms are required to fit an experimental FID curve.

More recently, Lee, Tse, Goldburg, and Lowe[6] and independently Evans and Powles[7] showed by iteration of an equation of motion for the magnetization that the FID function could be written as

$$F(t)=F_0(t)+F_1(t)+F_2(t)+\cdots, \tag{2}$$