Ferromagnetic and antiferromagnetic spin correlation in mictomagnets

Paul A. Beck*
University of Illinois, Urbana, Illinois 61801
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Typical mictomagnetic (spin-glass) behavior, as in Cu-Mn alloys, depends on the presence side by side of regions with predominantly ferromagnetic spin correlation (magnetic clusters) and a matrix with predominantly antiferromagnetic spin correlation. The volume fraction occupied by these two magnetic structures in different mictomagnetic alloys varies from practically zero of one to zero of the other. As the volume of ferromagnetically correlated regions approaches zero the susceptibility cusp and the saturated spontaneous magnetization after field cooling to low temperatures tend to disappear, while the displacement (shift) of the magnetization curve on field cooling becomes very large. At the other extreme, where the volume fraction with predominantly antiferromagnetic spin correlation approaches zero, the displacement of the magnetization curve and the unidirectionality of the remanence after field cooling disappear and the "freezing temperature" becomes frequency dependent.

INTRODUCTION AND RESULTS

It is well known that typical mictomagnets, e.g., *Cu*-Mn alloys, show certain characteristic features, such as (a) cusp in the alternating low-field susceptibility versus temperature curve at T_f, (b) "viscous" magnetic behavior with time dependence of the magnetization and thermomagnetic history effects in a temperature range around roughly $T_f/3$, and (c) unidirectional remanence at and below about $T_f/30$, after field cooling to that temperature.

It is also known that in *Cu*-Mn alloys with 9 to 25 at.% Mn magnetic clusters, with predominantly ferromagnetic spin correlation,[1,2] coexist with a matrix having predominantly antiferromagnetic spin correlation. The magnetic clusters, representing at most about 7% of the Mn atoms and thus approximately also of the volume in these quenched *Cu*-Mn alloys, correspond to small regions with $TiAl_3$-type atomic order.[3] Within these small ordered regions there are, therefore, ideally no Mn-Mn nearest neighbors and the Mn moments are aligned with one another ferromagnetically. It was first noted by Kouvel[4] that partial compensation of the Mn moments due to short-range antiferromagnetic coupling (presumably between nearest neighbors, mostly in the matrix) persists in $Cu_{76}Mn_{24}$ to temperatures well above T_f and that it manifests itself in the "paramagnetic" state by a decreased Curie constant. Later work showed a drastic further decrease of the Curie constant at temperatures well above T_f with increasing Mn content[5] above 25 at.% and also with plastic deformation.[6] That these effects are indeed resulting from antiferromagnetic coupling of Mn moments and not from the weakening or the disappearance of localized moments due to "broadening of a CPA-like Mn *d* band"[7] is strongly suggested by Kouvel's observation[4] that the Curie constant of $Cu_{76}Mn_{24}$ becomes higher above 320 K, where the antiferromagnetic coupling apparently breaks down, as well as by recent ıtron polarization analysis results.[8] The latter indicate also that the "average" spin correlation changes from ferromagnetic to antiferromagnetic in Cu-Mn alloys with higher Mn contents, i.e., the volume fraction of the matrix with short-range antiferromagnetic spin correlation becomes larger here at the expense of that of the magnetic clusters, as concluded earlier from magnetic measurements.[5] Even at Mn contents above 70 at.%, where Cu-Mn alloys have long-range antiferromagnetic spin order, the occurrence of short-range antiferromagnetism well above the Néel temperature is indicated by neutron diffuse scattering[9] near (100). This further supports the presence of perfectly healthy localized moments in these alloys and the validity of Kouvel's interpretation.

Recent work[10] with fcc *Co*-Mn alloys shows that here a limiting condition of cluster-free mictomagnetism can be at least approached, and that it leads to the near disappearance of some of the characteristic features of mictomagnetism mentioned above. Figure 1 shows the alternating low-field susceptibility index $S(T)$ for three alloys with 33 to 39 at.% Mn. The very drastic decrease of the peak of the temperature-dependent susceptibility, $S_f - S_0$, with increasing Mn content is plainly visible. By least-squares fitting of the parameters in Eq. (1) to pairs of

adjacent magnetization versus field isotherms $\sigma(H)$

$$\sigma(H,T)=\left[\chi'+\frac{c}{T-\theta}\right]H+\mu cB\left[\mu,\frac{H+\lambda(\sigma-\chi'H)}{T}\right] \tag{1}$$

above T_f, it was possible to obtain values for the "average" magnetic cluster moment, μ, and its concentration, c. Figure 2 shows the decrease of both μ and S_f-S_0 with increasing Mn content. The data are consistent with the extrapolation of both quantities to zero at approximately 41 at.% Mn. The absence of magnetic clusters leads at this composition to the effective disappearance of Langevin paramagnetism, since effectively all Mn moments are compensated by short-range antiferromagnetic coupling. The latter is indicated by the very pronounced neutron diffuse scattering near (100), observed in $Co_{59}Mn_{41}$.[11] It appears quite possible that the Co atomic moments are practically zero at this composition, although the extremely large magnetic cluster moments in alloys with somewhat higher Co contents (Fig. 2) may well be due to clusters of Co moments. Figure 3 shows the low-field portion of the $\sigma(H)$ isotherm at 4.2 K for $Co_{60}Mn_{40}$ (quenched from 900 °C) measured after cooling to that temperature in a field of +50 kOe. This isotherm is within the experimental accuracy a straight line between +50 and −50 kOe. The remanence of $\sigma_r=0.0078$ emu/g represents the total moment of all magnetic clusters aligned by field cooling. Its value corresponds to only 0.0045% of the Mn atomic moments present in the alloy (if they are well aligned), assuming $\mu_{Mn}=4\mu_B$ and $\mu_{Co}=0$. This very small remanence is unidirectional. It does not change its sign by exposing the specimen at 4.2 K to a (reversed) field of −50 kOe; furthermore, there is no measurable hysteresis. The magnetic behavior of this specimen thus indicates that the few small magnetic cluster moments present are extremely solidly "frozen in" at 4.2 K. This behavior, including a displacement field larger than 50 kOe, is certainly consistent with the presence of very massive short-range antiferromagnetism and with the high T_f value suggested by extrapolation (Fig. 2) to 40 at.% Mn.

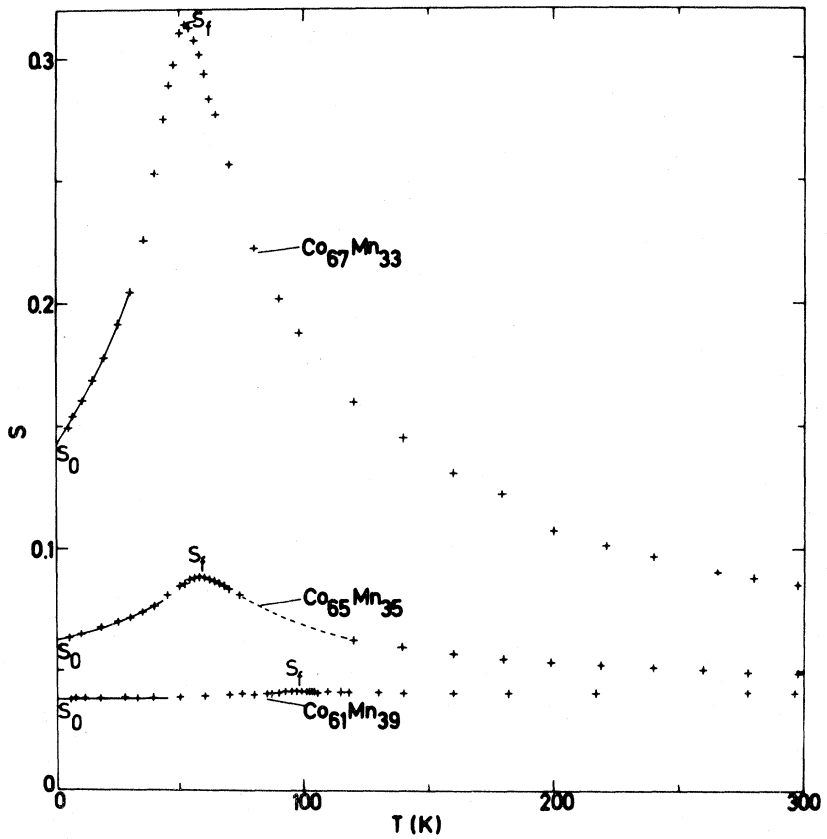

FIG. 1. Alternating low-field susceptibility index, S, vs temperature for quenched fcc Co-Mn solid solution alloys of compositions indicated. The height of the susceptibility maximum, S_f-S_0, decreases drastically with increasing Mn content. From Ref. 10.

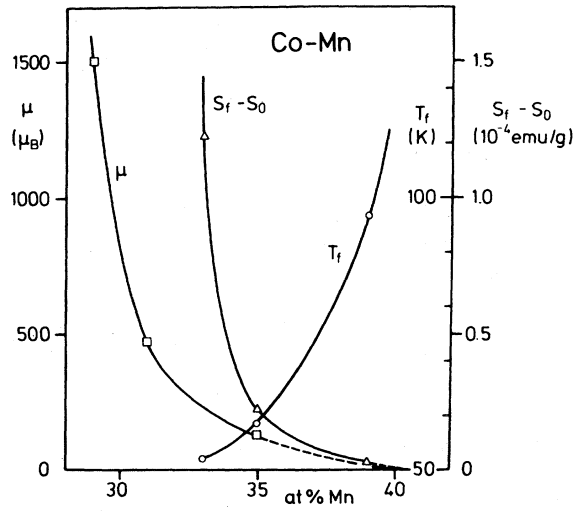

FIG. 2. $S_f - S_0$ and the "average" cluster moment, μ, vs Mn concentration. Data from Ref. 10.

If the predominance of the matrix at the expense of magnetic clusters leads to near disappearance of the susceptibility cusp and of the remanence, it is interesting to consider what deviations from the typical mictomagnetic features occur in the other limiting situation, where all localized moments participate in magnetic clusters and there is no matrix with antiferromagnetic spin correlation. Recent work with fcc *Au*-Fe alloys[12] indicates that in quenched $Au_{85}Fe_{15}$ the magnetic clusters predominate and a matrix is either absent or at least very ineffectual because of the lack of antiferromagnetic spin correlation. Thus, although this alloy may be considered a (borderline) mictomagnet, it was found[12] to show no unidirectional remanence upon cooling in a field of 50 kOe to 1.6 K.

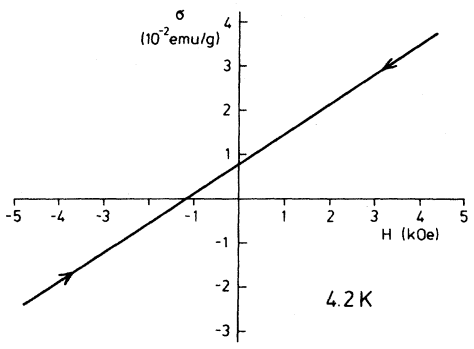

FIG. 3. Low-field region of magnetization, σ, vs applied field, H, isotherm at 4.2 K after cooling in a field of 50 kOe, for arc melted $Co_{60}Mn_{40}$ specimen plastically deformed, annealed at and quenched from 900 °C. This isotherm is, within the experimental accuracy, a straight line from +50 to −50 kOe. Ascending and descending branches are exactly superimposed: no hysteresis.

$Au_{82}Fe_{18}$ was described in the literature as ferromagnetic in the upper part of the temperature range of the susceptibility hump, but this interpretation was recently questioned.[12] In order to investigate this problem further, it was decided to study the effect of a change in the demagnetization factor.[13] For this purpose the magnetization of an approximately circular ~ 5-mm-diam thin disk, cut from the thin sheet specimen described earlier,[12] was measured in the present work, using a field of 10 Oe between 1.6 and 210 K at ascending temperatures after cooling to 1.6 K in zero field (the residual field of the superconducting coil and the earth's field were compensated). After reaching 210 K, the measurements were repeated with the temperature descending. In Fig. 4 curves (a) show the results with the plane of the thin specimen oriented parallel to the field direction (very low demagnetization factor) and curves (b) give the data for the same specimen mounted perpendicularly to the field direction (high demagnetization factor). The large thermomagnetic history effect [indicated by the discrepancy between the ascending (→) and the descending (←) temperature branches of curve (a) over the temperature range of the hump, and even somewhat above it] is consistent with mictomagnetism in this entire temperature range. The large shift (from ~ 45 to ~ 6 K) of the lower temperature of maximum curvature on changing the orientation of the specimen from parallel [curve (a) →] to perpendicular [curve (b) →] with respect to the field direction proves that this temperature is codetermined by the demagnetization factor, so that it does *not* correspond to an intrinsic magnetic feature, such as the magnetic phase transition previously reported.[14] The same consideration applies also to the upper temperature of maximum curvature in curve (a) → near 144 K, which shifts to near 173 K in curve (b) →, as well as to the temperature of the inflection point in curve (a) → near 185 K, which shifts to about 200 K in curve (b) →. Since the same specimen was used for the measurements with both high and low demagnetization factor, the observed temperature shifts cannot be attributed to differences in the metallurgical conditions. Consequently, *neither the upper temperature of maximum curvature nor the inflection point can possibly correspond to a Curie temperature.* Thus, the bulk magnetic measurements described do not give any support for the suggestion[14] that quenched $Au_{82}Fe_{18}$ is ferromagnetic in the upper temperature range of the hump and that on cooling it undergoes a magnetic phase transition from the ferromagnetic to the "spin-glass phase."

Magnetization versus field isotherms were measured in 10-K intervals from 70 to 170 K for the thin sheet (quenched) $Au_{82}Fe_{18}$ specimen previously described,[12] using a vibrating specimen magnetometer

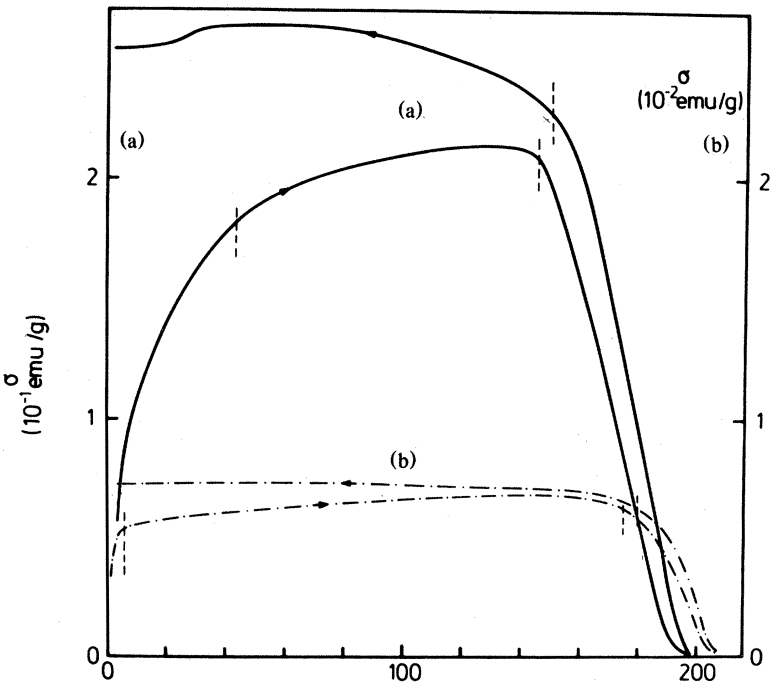

FIG. 4. Magnetization vs temperature for an approximately circular specimen of $Au_{82}Fe_{18}$, approximately 0.15 mm thick, weighing 0.0164 g, cut from a thin rolled sheet, annealed at and quenched from 900 °C. Graphs (a) give the magnetization with the specimen oriented parallel to the field direction. Lower graph (a) → measured with specimen temperature increasing after zero-field cooling to 1.6 K; upper graph (a) ← with specimen temperature decreasing. Dash-dot graphs (b) obtained in the same way, but with specimen oriented perpendicularly to field direction. Note the factor of 10 between the magnetization scales for (a) and (b). All measurements in field of 10.3 Oe.

and automatic continuous recording with the field increased automatically at a uniform low rate, after zero-field cooling from 300 K to each measuring temperature. As seen in Fig. 5 the curves do not show saturation. They follow each other in a very regular manner, without any noticeable change in this regularity at the reported[14] "Curie temperature" of 155 K. Equation (1) was least-squares fitted to each pair of consecutive isotherms. Note that the common fit for the isotherms at 150 and 160 K, which straddle the reported "Curie temperature," turned out to be particularly excellent, with (the root-mean-square

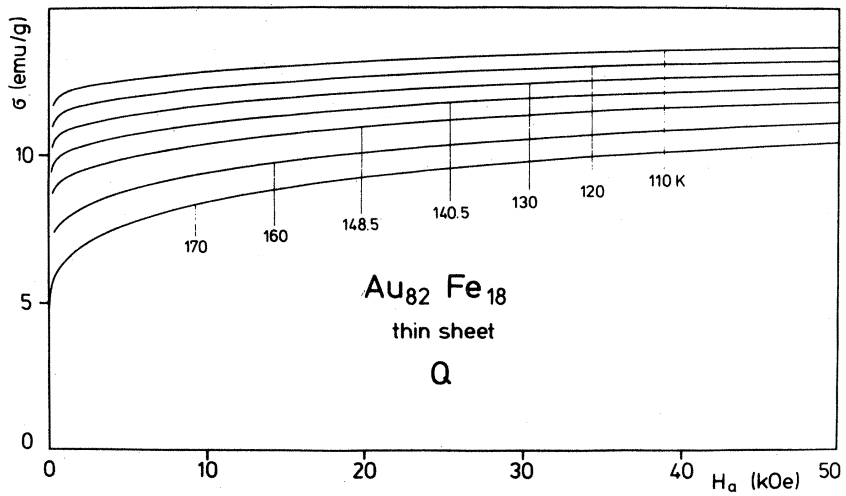

FIG. 5. Magnetization vs applied field isotherms at temperatures indicated, for elongated thin sheet specimen of $Au_{82}Fe_{18}$ (Ref. 12) oriented parallel to field. The $\sigma(H)$ curves were recorded with slowly increasing field, after zero-field cooling from 300 K to each measuring temperature.

fractional deviation) RMSFD is equal to 0.001 87. But the fit was very good in the entire temperature range and the RMSFD showed no systematic variation with the temperature. This is all the more remarkable, since in the temperature range used, $Au_{82}Fe_{18}$ has its susceptibility hump and it exhibits the magnetic "viscosity" effects referred to above.

The results, Fig. 6, show that the "average" cluster moment, μ, increases from 30 to $180\mu_B$ with decreasing temperature, while the total cluster magnetization, μc, remains essentially constant at about $0.5\mu_B$ per alloy atom. Even if it is assumed that all Fe moments participate in magnetic clusters, this μc value requires an Fe atomic moment of $\mu_{Fe}=2.78\mu_B$, which is rather large in comparison with dilute alloy data. A check was, therefore, made by measuring the saturated spontaneous magnetization in $Au_{82}Fe_{18}$ at 1.6 K. Figure 7 gives the magnetization versus field after the spherical specimen, described previously,[2] was cooled to that temperature in a field of 50 kOe. The dashed line, drawn tangent to the high-field end of the descending magnetization curve, intersects the σ axis at a value of 13.8 emu/g. This corresponds to a total cluster magnetization of $0.42\mu_B$ per alloy atom. Since this value results from measurements at 1.6 K, its agreement with the $0.5\mu_B$ per alloy atom value, derived in an entirely different way from 70–170-K data, may be considered quite satisfactory. But it is somewhat lower than the latter, so that it gives a more reasonable Fe moment of $\mu_{Fe}=2.35\mu_B$, assuming again that all Fe moments participate in magnetic clusters. The assumption that not all Fe moments are in magnetic clusters would lead to higher μ_{Fe} values, which are improbable. In the same way the saturated spontaneous magnetization was also measured at 1.6 K for quenched $Au_{85}Fe_{15}$ after cooling in a field of 50 kOe. The value of 7.14 emu/g obtained, together with $\mu_{Fe}=2.35\mu_B$, gives 64% for the fraction of Fe moments aligned by field cooling, i.e., participating in magnetic clusters. This result is again in reasonable agreement with the 73% participation derived from $\sigma(H)$ data for 60 to 200 K by means of least-squares fitting of Eq. (1), as in Ref. 12, but now using the value of $\mu_{Fe}=2.35\mu_B$.

Figure 7 shows that quenched $Au_{82}Fe_{18}$ does not exhibit unidirectional remanence at 1.6 K, after being cooled to that temperature in a field of 50 kOe. Since this alloy shows thermomagnetic history effects at least up to about 200 K (Fig. 4), the absence of unidirectional remanence is here demonstrated to temperatures lower than 1/100 of the upper limit of mictomagnetism. The absence of this characteristic feature of mictomagnetism is here, as in $Au_{85}Fe_{15}$,[12] associated with the predominance of magnetic clusters and with the lack of a matrix having antiferromagnetic spin correlation. It has been already noted[2] on the basis of earlier data by Kouvel[15] that the magnitude of the displacement (shift) of the hysteresis loop upon field cooling increases with the ex-

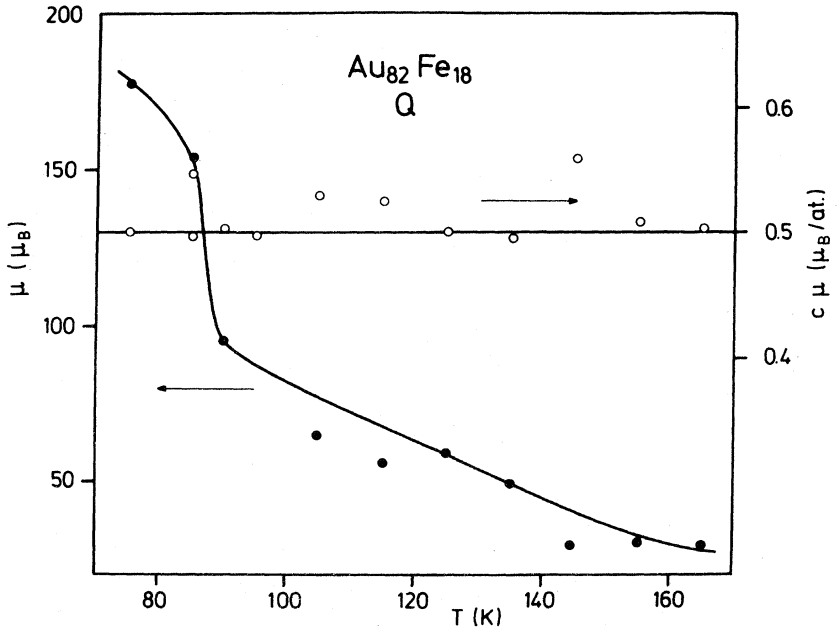

FIG. 6. "Average" magnetic cluster moment, μ, and total cluster moment, μc, per alloy atom vs temperature, from least-squares fitting of Eq. (1) to pairs of consecutive $\sigma(H)$ isotherms for thin sheet speciment of $Au_{82}Fe_{18}$, as in Fig. 5.

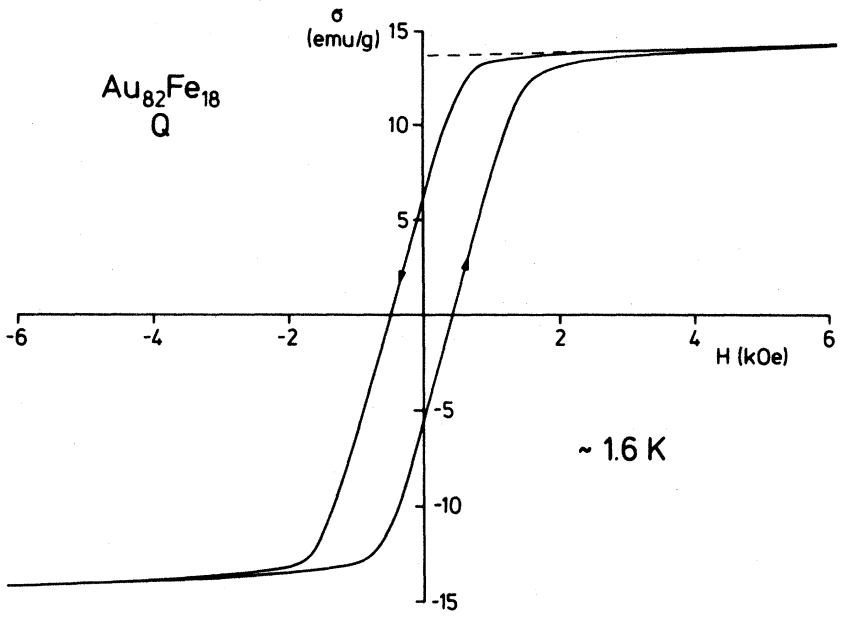

FIG. 7. Hysteresis loop at 1.6 K, σ vs applied field, H, for spherical $Au_{82}Fe_{18}$ specimen severely deformed, annealed at and quenched from 900 °C. Specimen cooled from 300 to 1.6 K in a field of 50 kOe.

tent of short-range antiferromagnetism in Cu-Mn alloys. The present findings for $Au_{82}Fe_{18}$ represent an extrapolation of this relationship to the effective absence of a short-range antiferromagnetic matrix, while the results here reported for $Co_{60}Mn_{40}$ demonstrate an extrapolation to the opposite extreme where effectively all Mn moments belong to the short-range antiferromagnetic matrix.

DISCUSSION

As summarized in Table I, the fraction of the atomic moments which participate in magnetic clusters in mictomagnetic alloys varies from near zero to 100%. We have seen that these differences in magnetic structure have a profound influence on certain aspects of magnetic behavior. In the following, we will examine to what extent they are correlated with the widely varying frequency dependence of T_f in mictomagnetic alloys.

The Cu-Mn alloys occupy an intermediate position in regard to the prevalence of magnetic clusters, Table I. Depending on the composition, the fraction of Mn moments in magnetic clusters varies from less than 1% to a few percent. Most of the Mn moments by far are in the matrix, which occupies most of the volume. The hyperfine splitting observed[16(a)] in the Mössbauer spectrum of the small amounts of ^{57}Fe or ^{119}Sn, diffused into the Cu-Mn alloys in order to serve as probes, defines the temperature below which the antiferromagnetically coupled Mn moments of the matrix are frozen for periods of time of the order of at least about 10^{-7} sec. It was found by Window[16(a)] that the freezing process for these moments is very abrupt, taking place in a very narrow temperature range, as revealed by the evolution of the Mössbauer hyperfine splitting upon cooling. Consequently, measurements with even widely different time resolution give "freezing temperatures,"

TABLE I. Saturated spontaneous magnetization data at 4.2 K (a) or 1.6 K (e), and the total cluster moment calculated from paramagnetic data for 50 and 60 K (d) give the percent of atomic moments present in each alloy participating in magnetic clusters, assuming that (b): $\mu_{Co}=0$, (c): $\mu_{Mn}=4\mu_B$, and (f): $\mu_{Fe}=2.35\mu_B$.

Alloys (quenched)	Total cluster moment per magnetic atom (μ_B)	Percent of atomic moments Aligned by field cooling
$Co_{60}Mn_{40}$	0.00018[a]	0.005[b,c]
$Cu_{91}Mn_9$	0.027[d]	0.68[c]
$Cu_{88}Mn_{12}$	0.26[a]	6.5[c]
$Cu_{75}Mn_{25}$	0.135[a]	3.4[c]
$Cu_{34}Mn_{66}$	0.000 49[a]	0.019[c]
$Au_{85}Fe_{15}$	1.5[e]	64[f]
$Au_{82}Fe_{18}$	2.35[e]	100[f]

which are for practical purposes identical. Thus, for the frequency range used in the alternating field susceptibility measurements (0.5 to 1000 Hz) in determining the cusp temperature, T_f was found to be essentially frequency independent in Cu-Mn alloys[1] and the T_f values were also in good agreement with the Mössbauer hyperfine splitting temperatures.[2,16(a)] Although the bulk susceptibility of these alloys is dominated by the reaction of the magnetic clusters to the field, this reaction and, therefore, also T_f are apparently controlled by the freezing of the Mn moments of the matrix, which are compensated by antiferromagnetic coupling to each other. That this short-range antiferromagnetic coupling in $Cu_{32}Mn_{68}$ is present even at temperatures very much higher than T_f is shown by the neutron diffuse scattering near (100) reported by Vance *et al.*[9] For more dilute *Cu*-Mn alloys diffuse neutron scattering information as a function of temperature is at present not available. However, it view of recent results by Monod *et al.*[17] it seems not unreasonable to assume that in Cu alloys even with only 0.5 or 0.06% Mn there are magnetic clusters present (although in these dilute alloys the clusters may consist only of pairs or triplets of ferromagnetically coupled Mn moments) surrounded by a matrix with predominantly antiferromagnetic spin correlation. These workers found unidirectional remanence in such dilute alloys after field cooling to sufficiently low temperatures, in close analogy to the behavior of concentrated alloys.

It is well known[15] that Ag-Mn alloys show mictomagnetic behavior just like that of Cu-Mn alloys. It was recently found[18] that here, too, T_f is independent of frequency up to 10^3 Hz, presumably also because of the unexplained abruptness of the freezing of the compensated Mn moments of the matrix and the interaction between these frozen moments and the magnetic clusters. This interaction, although clearly present in *Cu*-Mn and *Ag*-Mn alloys,[2] is also not well understood as yet.

It was pointed out[2] that, in contrast to the behavior of *Cu*-Mn alloys, in *Au*Fe alloys a great discrepancy, amounting up to a factor of 28 at low Fe concentrations, is found between the Mössbauer hyperfine splitting temperatures and the low steady-field susceptibility cusp temperatures. A discrepancy, although smaller, is present also at high Fe concentrations. The interpretation[2] given in terms of frequency dependence is consistent with the present results. In $Au_{82}Fe_{18}$ all Fe moments are in magnetic clusters, so that not only the bulk magnetic susceptibility, but also the hyperfine splitting in the Mössbauer spectrum relates directly to the behavior of magnetic clusters. In the absence of a matrix with antiferromagnetic spin correlation, the freezing of the clusters takes place much more gradually than that of the antiferromagnetically coupled Mn moments, in accordance with the Néel model, which provides for frequency dependence.[19] For $Au_{90}Fe_{10}$ the frequency dependence, although rather small in the frequency range studied (9 to 1300 Hz), has been definitely established by Tholence.[20] The rather abrupt development of the Mössbauer hyperfine splitting in *Au*-Fe with decreasing temperature, reported by various investigators [see for instance Ref. 16(b)], remains as yet unexplained. However, it does appear from the available information that a marked frequency dependence of T_f is associated with the effective absence of a matrix with antiferromagnetic spin correlation.

If the above considerations are correct, one may expect that for various metallic and insulating mictomagnets, for which the cusp temperature was found to show a pronounced frequency dependence, will show no unidirectional remanence after field cooling to temperatures near $T_f/30$. Vice versa, the cusp temperature for those mictomagnets, which are known to exhibit unidirectional remanence after field cooling, may be expected to be essentially frequency independent.

It was found that aging[5] and plastic deformation[6] give rise to changes in the magnitude of the susceptibility near the cusp for $Cu_{75}Mn_{25}$ by changing the moment and the concentration of the magnetic clusters, but they have only a minor effect on T_f. In the light of the above findings, one may expect much larger changes in T_f by altering the size of the magnetic clusters in alloys, such as *Au*-Fe, which have effectively no matrix with antiferromagnetic spin correlation. In fact, the flat-topped hump in the susceptibility versus temperature curve under conditions where there is no limitation by the reciprocal demagnetization factor,[12] may well be due to the particular size distribution of the magnetic clusters in a given specimen. This is certainly suggested by recent results of Crane and Claus,[21] showing a large effect of aging treatments on the temperature range of the hump for $Au_{86}Fe_{14}$ and $Au_{85}Fe_{15}$.

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*Present address: Institut für Atom- und Festkörperphysik, Freie Universität Berlin, Boltzmannstr. 20, 1000 Berlin 33, G.F.R.

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