Spin clusters and random local anisotropy in mictomagnetic Au-Fe alloys

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On the basis of magnetic measurements, the magnetic specific heat, Mössbauer spectra, and neutron magnetic scattering data, a model is presented for the magnetic structure of the fcc gold-iron alloys with 0.15 to 0.19 atomic fraction Fe which is more consistent with the various types of data than are previous models. The model explains some previously unexplained experimental results.

INTRODUCTION

Up to an Fe concentration of ≈ 0.1 atomic fraction the fcc Au-Fe solid solution alloys are generally recognized[1,2] as spin-glass-like in their magnetic behavior (e.g., time-dependent magnetization) below the temperature T_F of the low-field susceptibility maximum. Recent careful work by Wagner and Gonser[3] confirmed the observation[4] that over a range of concentrations, the temperature T_M of the onset of hyperfine splitting in the Mössbauer spectra is consistently higher than T_F, although both of these temperatures refer to phenomena connected with the crossover from paramagnet to spin glass. Also, several recent studies[5-7] clearly show that T_F itself varies for a given alloy, depending on the frequency of the alternating field used for the measurements. Thus, the observed temperature of the crossover depends on the characteristic time of the measurement used, so that this crossover cannot be considered as a "magnetic phase transition." Instead, it seems to be a smeared-out dynamic effect, such as was found by Mezei[8] for the spin glass to paramagnet crossover in a Cu-Mn alloy by means of neutron spin-echo measurements. It is apparently also well recognized[9,10] that spin clusters with predominantly ferromagnetic spin correlation are responsible for the magnetic behavior of Au-Fe alloys with ≈ 0.1 to 0.15 atomic fraction Fe. However, no general agreement has been reached as yet with regard to the nature of the magnetic behavior of the Au-Fe alloys with Fe contents between ≈ 0.15 and 0.20. According to a rather widely held view, these alloys undergo upon cooling a double magnetic phase transition from paramagnet to ferromagnet and from ferromagnet to spin glass. In the present paper the relevant information available from different types of experimental data is reviewed and it is shown that no spacially and temporally long-range ferromagnetism occurs in the alloys concerned. A new model is presented, which is consistent with the various experimental results and which is capable of explaining, at least qualitatively, some previously unexplained features of the experimental data.

MAGNETIC DATA

Coles, Sarkissian, and Taylor[10] found by means of alternating low-field, as well as low-steady-field measurements that the external mass susceptibility $\chi_e = \sigma/H_a$ (where σ is the magnetization per unit mass and H_a is the applied field) of quenched Au-Fe alloys with 0.17 to 0.23 atomic fraction Fe is in a certain temperature range approximately temperature independent. This is a result of limitation of the external susceptibility by the reciprocal demagnetization factor $1/D$ when the low-field internal susceptibility $\chi_i = \sigma/H_i$ is large. Since the internal field is $H_i = H_a - D\sigma$, it follows that $\chi_e = (\chi_i^{-1} + D)^{-1}$. If χ_i is much larger than $1/D$ this gives $\chi_e \approx 1/D$, which is essentially temperature independent. Coles *et al.* interpreted their results, as usual at the time, in terms of long-range ferromagnetism in the temperature range where χ_e is "demagnetization controlled." They considered the upper temperature limit of this range as the Curie temperature T_C. The lower limit of this temperature range, designated T_F, was thought to correspond to a second magnetic phase transition. Fully aware of the important role of magnetic clusters in these alloys, Coles *et al.* proposed a model in which only a certain undetermined volume fraction of the alloy specimen was ferromagnetic between T_C and T_F and this "infinite cluster" coexisted with finite clusters located in the remainder of the volume. Below T_F the finite clusters were supposed to be frozen and to give rise to spin-glass-like behavior, but to be still coexisting with the ferromagnetic infinite cluster. The presence of finite magnetic clusters in $Au_{90}Fe_{10}$, $Au_{87}Fe_{13}$, and $Au_{85}Fe_{15}$ was well documented by the temperature-dependent low-angle neutron scattering found by Murani.[11]

Using a thin disk-shaped specimen of $Au_{82}Fe_{18}$ as quenched and turning it either parallel or perpendicular to the applied field it was possible to make susceptibility measurements as a function of temperature on the same specimen with two widely different demagnetization factors.[12] The results, shown in Fig. 1, indicate that both T_C and T_F shift markedly with the change in the demagnetization factor. The pronounced dependence on purely geometrical conditions of both the upper and the lower end of the temperature range where the susceptibility is demagnetization controlled clearly demonstrates that *the interpretation of these end points as magnetic phase-transition temperatures T_C and T_F cannot be correct.* Since the relationship $\chi_e = (\chi_i^{-1} + D)^{-1}$ gives an approximately temperature-independent χ_e as long as $\chi_i \gtrsim 2/D$, a relatively low susceptibility, such a demagnetization controlled χ_e by no means necessarily indicates the presence

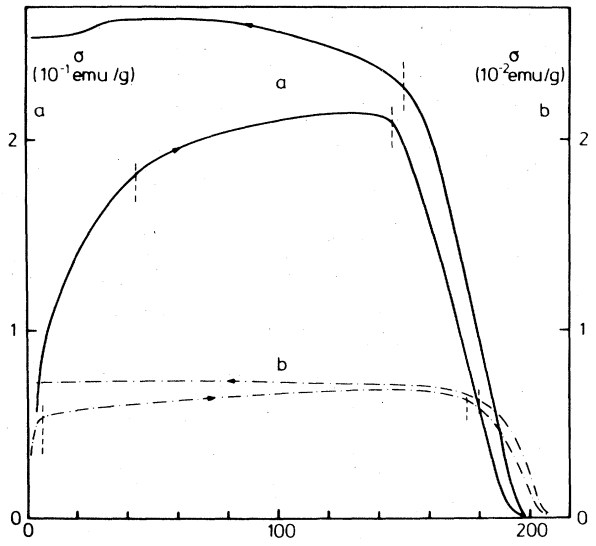

FIG. 1. Magnetization at a field of 10 Oe of a thin disk-shaped specimen of $Au_{82}Fe_{18}$, as-quenched, *a* with field parallel to the disk, *b* field perpendicular to the disk. Arrow pointing right: measured with temperature increasing from 4.2 to 220 K after zero-field cooling from 300 K. Arrow pointing left: with temperature decreasing from 220 K. Note the factor of 10 difference between ordinate scales for *a* and *b*. From Ref. 12.

of long-range ferromagnetism. The magnitude of χ_i needed for χ_e to be demagnetization controlled at low fields depends on D, that is on the shape of the specimen. χ_i values of the required magnitude may well result for instance from the low-field Langevin paramagnetism of a sufficiently high concentration of magnetic clusters with sufficiently large moments at sufficiently low temperatures. It is seen in Fig. 1 that in graph *a* (low demagnetization factor) the temperature range of the demagnetization controlled segment is much smaller than in graph *b* (high demagnetization factor). Also, the top of curves *a* is much more rounded than the top of curves *b*. Clearly, the χ_e values reached near the maximum of the decreasing temperature branch of curve *a* are approaching χ_i. In fact, approximating the thin disk used in this experiment with an oblate spheroid, one can calculate $D \approx 6.11$ g/cm^3 and, with this, one obtains for $\chi_e = 0.0265$ emu/g at the maximum $\chi_i \approx 0.0316$ emu/g, which is only about 17% larger than χ_e. This low χ_i value indicates that χ_e, measured at a large demagnetization factor, may well be largely limited by the reciprocal demagnetization factor over an extended range of temperatures without necessarily requiring the occurrence of long-range ferromagnetism.

Another result[12] shown in Fig. 1 is the large increase of the magnetization along the descending temperature branch of *a*, as compared with the ascending temperature branch. Clearly, graph *a* indicates a very considerable magneto-thermal-history effect, characteristic of spinglass or mictomagnetic behavior, as found previously for $Au_{85}Fe_{15}$ by Murani.[9] The significant fact is that this spin-glass behavior is encountered in quenched $Au_{82}Fe_{18}$ in the entire so-called "ferromagnetic" temperature range; it is not limited to temperatures below T_F. Such a large magneto-thermal-history effect was found[13] also with an aged (22 h at 200 °C) spherical specimen of the same alloy when measured in a field of 10 Oe, or less. That in $Au_{82}Fe_{18}$ this effect is certainly not due to remanence at temperatures above ~ 65 K is shown in the next paragraph. The low-field magnetic measurement results discussed indicate a rather close similarity between the alloys with 0.18 and with 0.15 Fe in regard to the temperature-dependence of the internal susceptibility. But because of the much higher χ_i maximum for $Au_{82}Fe_{18}$, the rounded form of this maximum is revealed by the measurement of χ_e only when a specimen configuration giving a very low D is employed, while for $Au_{85}Fe_{15}$ even a spherical specimen shows well[14] the rounded maximum of χ_e (which is not much different from χ_i), as well as the large magneto-thermal-history effect.

Detailed isothermal magnetization versus field data $\sigma(H)$ were obtained for $Au_{82}Fe_{18}$ in the temperature range of ~ 65 K to 195 K at intervals of ~ 10 K in both the quenched[12] and the aged[13] condition. These data, measured at first with increasing and then with decreasing fields at each temperature,[13] show a relatively small magneto-thermal-history effect and no remanence within the accuracy of the vibrating-sample magnetometer (VSM) instrument used. This means that the remanence, if any, at ~ 70 K is at least two orders of magnitude smaller than the magneto-thermal-history effect, measured in the low demagnetization arrangement, i.e., as the difference between the two branches of curve *a* at 70 K in Fig. 1. The isotherms have a marked curvature up to the top of the temperature range used and no saturation up to 50 kOe.[12] They form a very regular sequence and show no observable change in character on crossing T_C. The isotherms were least-squares fitted, as one would data for a "superparamagnet with interaction," using the expression $\sigma = \chi_0 H_i + \mu c B(\alpha,\mu)$, where χ_0 is a field-independent susceptibility, H_i is the internal field, μ is a representative cluster moment in units of Bohr magnetons, c is the cluster concentration per alloy atom, and $B(\alpha,\mu)$ is the Brillouin function expressed in terms of $\mu = gS$, assuming that $L \approx 0$. In order to take into account the magnetic interaction between the clusters and their magnetic environment in the molecular field approximation, the argument α of the Brillouin function has been changed from the usual $\alpha = H_i/T$ to $\alpha = (H_i + \lambda\sigma')/T$, where λ is the Weiss molecular field coefficient and $\sigma' = \sigma - \chi_0 H_i$, is the magnetization due to the clusters. The parameters χ_0, μ, c, and λ were determined by minimizing the root-mean-square deviation between the measured magnetization and σ calculated as indicated by the above expression from the measured H_i and T values for the data points along each pair of adjacent isotherms. (The curvature of an isotherm increases in a somewhat similar manner if either μ or λ becomes larger. By fitting data from two temperatures, rather than from only one, a much better separation of the effects of these two parameters is obtained.)

The fitting for the aged specimen was improved by using a better program and allowing more computer time. Furthermore, eliminating data points for $H_i < 1$ kOe at $T < 162$ K and also data points for $H_i < 2$ kOe at $T < 85$

K, which were markedly affected by the demagnetization factor, helped considerably in decreasing the root-mean-square fractional deviation. This improved fit resulted in a decrease of the μ values at low temperatures, as compared with the values previously published for the aged specimen.[13]

The new results for the cluster moment μ and the molecular field coefficient λ, as functions of the temperature, are shown in Fig. 2 for the aged specimen. It is significant that, although both quantities change considerably with the temperature, this change is gradual and they do not show any effect attributable to crossing T_C at 168 K. It should be noted that λ is positive, indicating ferromagnetic interaction between the cluster moments, but its values are two orders of magnitude smaller than that for Ni: 2992 mol/emu, as calculated from $\lambda=\Theta/C$ with the paramagnetic Curie temperature $\Theta=712$ K and the Curie constant $C=0.238$ emu deg/mol,[15] based on the (1102—1512)-K susceptibility data from Ref. 16. The equally low root-mean-square fractional deviations achieved in the fitting, namely 0.0022 ± 0.00025, both above the so-called "Curie temperature" and below it, indicate that within the experimental error *the magnetization can be quantitatively described in terms of superparamagnetism with interaction, without assuming any contribution from long-range ferromagnetism or infinite clusters.* This was found to be true in the entire temperature range studied: from $\sim$65 K to $\sim$195 K, which includes most of the temperature range where the low field external susceptibility of the spherical specimen was demagnetization controlled. The measurements were not extended below 65 K since remanence was found to occur at those temperatures.

According to the x-ray diffuse scattering results of Dartyge, Bouchiat, and Monod[17] in the quenched gold-iron

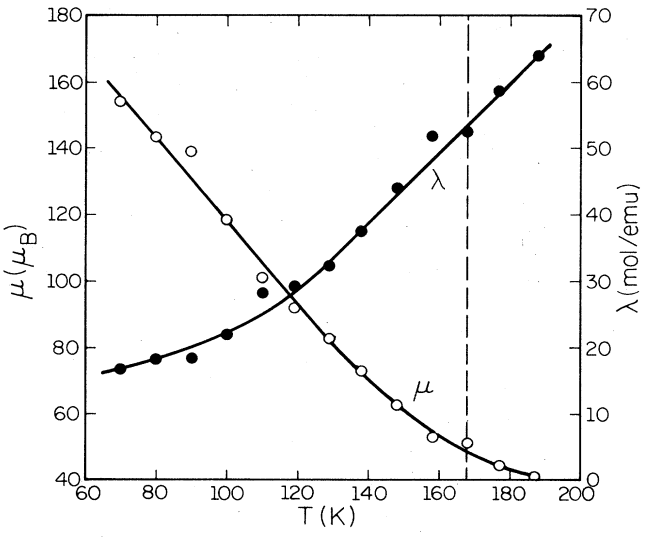

FIG. 2. Representative cluster moment μ and molecular field coefficient λ, for aged $Au_{82}Fe_{18}$, obtained by least-squares fitting (see text) to pairs of $\sigma(H)$ isotherms $\approx$10 K apart, shown in Fig. 4 of Ref. 13. Dashed vertical line indicates the so-called Curie temperature.

alloys with 0.144 to 0.19 Fe there is very extensive short-range segregation of the iron atoms in the form of platelets or Guinier-Preston (GP) zones consisting of pairs of adjacent (420)-type atomic planes and extending approximately 30 Å in directions parallel to these planes. The approximately 120 atoms in such a platelet are mostly Fe. The presence of spin clusters indicated by the magnetic measurements[12,13] suggest that the Fe moments within large portions of each platelet are ferromagnetically coupled with one another, presumably by nearest-neighbor interaction. The magnitude of the cluster moments μ shown in Fig. 2, can thus be accounted for by Fe atomic clusters in the GP zones.

MAGNETIC SPECIFIC HEAT

The magnetic specific-heat data recently published by Mirza and Loram[18] for quenched gold alloys with 0.02 to 0.23 Fe give significant further information regarding the nature of magnetism in these alloys. In agreement with previous data for the total specific heat, the new data show a broad maximum of the magnetic specific heat roughly 20 to 25 K above the temperature of the low field susceptibility maximum for the spin-glass alloys with 0.02 to 0.11 atomic fraction Fe. For the alloys with 0.15 and 0.18 Fe, Fig. 1 of Ref. 18 shows similar broad maxima about 30 to 35 K above the corresponding very low field susceptibility peaks interpolated by the authors using Sarkissian's critical peak temperatures.[19] The latter are very close to the T_C temperatures, as defined in Ref. 10. In the presence of long-range ferromagnetism or of an infinite cluster one should see a more or less sharp maximum of the magnetic specific heat at the Curie temperature. Figure 1 of Ref. 18 shows no perceptible maxima at T_C for the two alloys discussed. In fact, T_C is located for both alloys at near zero curvature of the specific heat versus temperature graph, not far from an inflection point. Thus one may conclude that the concentration of Fe moments participating in infinite clusters is imperceptibly small in the alloys with 0.15 and 0.18 Fe. This finding is, of course, in excellent agreement with the conclusion reached earlier by Murani[9] for $Au_{85}Fe_{15}$ and in Ref. 12 for $Au_{85}Fe_{18}$ on the basis of magnetic measurements, as discussed above. It is also quite apparent from Fig. 1 of Ref. 18 that, apart from the second maximum at $\sim$50 K (which is discussed further below), the temperature dependence of the magnetic specific heat for both alloys under consideration shows remarkable similarities with that for the spin-glass alloys of lower Fe contents. This again is consistent with the spin-glass-like magnetic behavior (large magneto-thermal-history effect) of both $Au_{85}Fe_{15}$ (Refs. 9 and 14) and $Au_{82}Fe_{18}$ (Refs. 12 and 13) in their entire temperature ranges of high susceptibility, as described above.

Doubling the Fe content from 0.02 to 0.04 leads roughly to doubling the maximum of the magnetic specific heat according to the data in Fig. 1 of Ref. 18. Increasing the Fe content from 0.15 to 0.18 (a 20% increase) results in an increase of the magnetic specific heat maximum by $\sim$25.8%, a rate of increase only $\sim$30% larger than that between 0.02 and 0.04 Fe, suggesting that even at 0.18 Fe

most of the magnetic specific heat comes from the thermal breakdown of the intracluster spin correlation. However, increasing the Fe content from 0.18 to 0.23 (a 27.8% increase) results in a 129% increase in the magnetic specific-heat maximum. This represents an increase more than three times larger than that between 0.15 to 0.18 Fe, when compared on the basis of the same percentage increase of the Fe content. Even such a very rough comparison shows clearly that the intercluster interaction makes a much larger contribution to the magnetic specific heat at Fe contents above ~ 0.18 than below this concentration; the system is gradually coming closer to long-range ferromagnetism. That it does not actually become ferromagnetic, however, is indicated by the presence of a component in the magnetic specific heat of the 0.23 Fe alloy having a maximum at ~ 50 K, as shown in Figs. 1 and 2 of Ref. 18. This matter is more fully discussed further below.

CRITICAL SUSCEPTIBILITY

By using needle-shaped specimen with a very low demagnetization factor and extremely small alternating fields, Sarkissian succeeded in demonstrating[19] critical behavior in Au-Fe alloys with 0.16 to 0.28 Fe at the onset of ferromagnetism, assumed in his paper to be long range, involving infinite clusters. His susceptibility data are presented in the form of graphs covering temperature ranges of 180 or 360 K, which do not allow evaluation of the sharpness of the peak at temperatures closer than 1 or 2 K to the peak. It is, therefore, not possible to estimate reliably on the basis of the published data the size of the fluctuating regions $\xi = a_0 \epsilon^{-\nu}$ within which ferromagnetic spin correlation prevails.[20(a)] Assuming $\nu = 0.64$ (three-dimensional Ising model[20(b)]), $a_0 = 2.83$ Å (the nearest-neighbor distance of atoms in $Au_{82}Fe_{18}$), and $\epsilon = (T - T_c)/T_c = 0.0066$ (based on the estimated width of the critical susceptibility peak for the alloy with 0.185 Fe in Ref. 19) gives the rough estimate of $\xi = 70$ Å. This value suggests that the critical behavior observed by Sarkissian may be due to the onset of ferromagnetism in regions of the order of magnitude of the GP zones, consisting predominantly of segregated Fe atoms.[17] At any rate, the published data do not actually provide evidence for the existence of infinite clusters or for long-range ferromagnetism. That infinite clusters are in fact not formed here is confirmed by the absence of a magnetic specific-heat peak at the temperature T_c of the critical susceptibility peak for the 0.18 Fe alloy, as discussed above.

NEUTRON SCATTERING

In apparent contradiction with the above conclusions from magnetic and specific-heat results, Murani discovered by means of inelastic neutron scattering[21] the presence of spin waves in $Au_{81}Fe_{19}$ and considered this as evidence for long-range ferromagnetic order. However, in the same paper he also reported spin waves in $Fe_{70}Al_{30}$, although it is now clear that this alloy with Fe_3Al-type of long-range atomic order is not ferromagnetic despite its demagnetization limited external susceptibility between 200 and 400 K, as measured in a 50-Oe steady field.[22] Measurements with an alternating field of 3-Oe amplitude show a round susceptibility maximum that is *not* demagnetization limited.[22] It appears that the 50-Oe steady field internal susceptibility around its maximum exceeds the reciprocal demagnetization factor of the spherical specimen, while the maximum of the alternating low field internal susceptibility for the same specimen remains below this limit. The absence of long-range ferromagnetism in $Fe_{70}Al_{30}$ is indicated also by the Mössbauer spectrum: At 295 K it shows a considerably broadened *single line,* while at 2.5 K, where the alloy is clearly in the mictomagnetic (spin-glass) state, the six split lines are well resolved.[23] Furthermore, low-angle neutron scattering shows the presence of large magnetic clusters in $Fe_{70}Al_{30}$ at all temperatures up to 500 K.[24] It is now clear that this alloy is not a long-range ferromagnet at any temperature, despite a view to the contrary expressed in the original publication[22] (somewhat hedged in view of the alternating field susceptibility results). The presence of spin waves in this alloy at 265 K shows that spin waves may occur in a superparamagnet with large cluster moments, so that they are no evidence for long-range ferromagnetism. The latter conclusion was reached quite generally, independently of $Fe_{70}Al_{30}$, by Aeppli *et al.*[25] Clearly then Murani's results[21] are compatible with the view that $Au_{82}Fe_{18}$ is not ferromagnetic, derived above from magnetic and specific-heat data.

MÖSSBAUER DATA

The excellent magnetization data of Crangle and Scott[26] plotted in the form of σ^2 versus H/σ isotherms (Arrott plots) led to the conclusion that the quenched gold-iron alloys with more than 0.11 Fe are ferromagnetic. However, the Curie temperatures derived by means of the otherwise very useful Arrott-plot method[27] are up to ~ 0.24 Fe systematically higher than the temperatures T_M, where hyperfine splitting starts in the Mössbauer spectra.[28] For $Au_{85}Fe_{15}$, the σ^2-versus-H/σ plots indicate a Curie temperature of 110 K, while T_M is 40 K and Murani[9] found by magnetization measurements that this alloy is not ferromagnetic at any temperature, but it is a mictomagnet. It appears that for the fcc gold-iron alloys, the magnetic properties of which are dominated by large spin clusters, the σ^2-versus-H/σ plot method does not give reliable results for the onset of long-range ferromagnetism. This may presumably come about because the high field magnetization, on which the method relies, reflects "field induced kinematic ferromagnetism," i.e., an appreciable degree of time-average alignment of the large cluster moments by steady fields of some kiloersteds. That this "alignment" is far from being a static one, however, is shown by the absence of hyperfine splitting in the Mössbauer spectrum in a range of temperatures below the "Curie temperature" indicated by the σ^2-versus-H/σ plot method. It is well known that the time-average hyperfine field over periods of $\sim 10^{-7}$ sec, H_{hf}, acting on ^{57}Fe nuclei must reach several kiloersteds in order to produce per-

ceptible hyperfine splitting. T_M is the temperature at which the thermal reorientations of the cluster moments become sufficiently slow to satisfy this condition.

It was discovered by Lauer and Keune[29] and independently also by Varret, Hamzic, and Campbell[30] that the Mössbauer spectra of fcc Au-Fe solid solutions with about 0.168 and 0.19 Fe, respectively, can be essentially completely polarized by an applied field of 20 and 6 kOe, respectively, (applied parallel to the incident γ ray) in a range of temperatures above ~ 50 K, but that below ~ 50 K the degree of polarization attained decreases considerably with decreasing temperature. These findings, as well as the additional increase of the hyperfine field ($H_{\rm hf}$) in excess of the values extrapolated from higher temperatures, also observed below ~ 50 K (in the absence of an applied field), were interpreted[29,30] in terms of the Gabay-Toulouse theory.[31] It was assumed that in a range of temperatures above ~ 50 K, a component of the Fe moments is frozen and aligned parallel to an applied field, so that the alloys are in effect ferromagnetic. At ~ 50 K, the transverse components of the Fe moments also freeze ("canting transition"), but remain randomly oriented within the perpendicular plane. These transverse components of the Fe moments were considered to be responsible for the spin-glass-like behavior (e.g., the magneto-thermal-history effect) below ~ 50 K. Spin-glass-like behavior was considered to coexist at these temperatures with the ferromagnetism associated with the aligned components of the Fe moments.

The following difficulties with the explanations[29,30] in terms of the Gabay-Toulouse theory should be noted. As discussed above, there is no experimental evidence for ferromagnetism or "infinite clusters" in $Au_{82}Fe_{18}$ at any temperature (either quenched or 200 °C aged). On the other hand, mictomagnetic behavior (large magneto-thermal-history effect) was found not only below 50 K, but even at temperatures far above it.[12,13] Also, the validity of the Gabay-Toulouse theory itself has been questioned.[25]

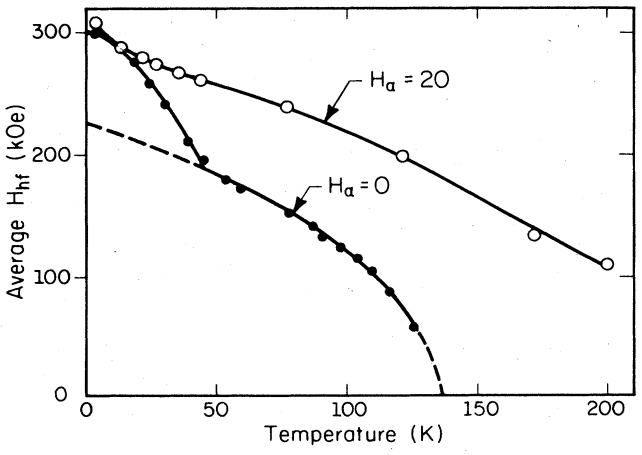

FIG. 3. Average hyperfine field $H_{\rm hf}$ from Mössbauer spectra as a function of temperature with 0 and 20 kOe field, respectively, applied to the quenched $Au_{83.2}Fe_{16.8}$ alloy specimen. Data from Ref. 32; in this figure the 20-kOe data are corrected for zero field.

In a recent paper Brand, Manns, and Keune[32] reported a very interesting new effect in the Mössbauer spectrum. When measured while an external field of 20 kOe was applied to a 16.8 at. % Fe alloy specimen, the hyperfine field $H_{\rm hf}$ had approximately the same magnitude at 4 to about 20 K as that without the applied field, see Fig. 3. Surprisingly, however, $H_{\rm hf}$ measured with the applied field on, had much *higher* values than without the applied field, not only at 50 K but even at temperatures up to and presumably also above 200 K i.e., well above ~ 140 K, the extrapolated approximate temperature where $H_{\rm hf}$ collapsed to zero in the absence of an external field. This behavior of the Au-Fe alloy is, of course, very different from that observed with ferromagnetic iron, where $H_{\rm hf}$ is *decreased* by the magnitude of the applied field and it goes to zero at the same temperature where it does without an applied field, namely at the Curie temperature. The fact that for the Au-Fe alloy the temperature of the collapse of the hyperfine field is greatly increased by an applied external field, as seen in Fig. 3, indicates that here this is not a Curie temperature but T_M, as defined above. The suggestion that the observed increase of $H_{\rm hf}$ results from an increase of the Fe atomic moments due to the external field,[32] appears to be quite improbable. Furthermore, it is not at all clear how the experimentally found[32] absence (when an external field is applied) of an additional increase of $H_{\rm hf}$ below ~ 50 K in excess of the values extrapolated from higher temperatures, as shown in Fig. 3, could be explained on the model[29,30] based on the Gabay-Toulouse theory. The latter assumes the freezing of the transverse components of the moments, and hence an increase in $H_{\rm hf}$, at ~ 50 K.

PROPOSED NEW MODEL

An alternative explanation of the decrease with decreasing temperature below 50 K of the degree of polarization attained by an external field in the gold-iron alloys discussed, which is not subject to the various difficulties mentioned above, was briefly referred to earlier.[33] It is based on the assumption of a quasi-random local anisotropy, which largely determines the local orientations of the cluster moments at low temperatures in the absence of an external field. At temperatures above ~ 50 K the cluster moments are freed by thermal activation from the constraints of the local anisotropy. They can be, therefore, quite extensively polarized by an applied field of 20 or 6 kOe in a range of temperatures just above ~ 50 K, as described in Refs. 29 and 30. With decreasing temperatures below ~ 50 K more and more cluster moments find the thermal activation insufficient to liberate them from the local anisotropy, so that the fraction of cluster moments locked into their quasirandom orientations increases. The model here described explains also the observation of Lauer and Keune[29] that the partial polarization due to a field of 20 kOe at 4.2 K disappears spontaneously when the field is removed, as shown by the Mössbauer spectrum; the cluster moments then largely return to their quasirandom orientations under the influence of the local anisotropy.

Because of the great anisotropy in the shape of the

Guinier-Preston zones or platelets with which the magnetic clusters are associated, one may expect the cluster moments to be subject to shape anisotropy. In each fcc crystal there are (420)-type planes in 12 different, but crystallographically equivalent, orientations. In a polycrystalline specimen the number of such plane orientations is so large that it may be considered quasirandom. The shape anisotropy may well be at least one of the components of the quasirandom local anisotropy postulated above. In view of the atomic structure of the (420) plane double layers, it seems quite possible that an additional magnetocrystalline anisotropy component provides favored directions for the cluster moments within the plane of the platelets, which is favored by the shape anisotropy. In amorphous alloys, where similar Mössbauer phenomena were found (32), the local anisotropy may be connected with a random string-like arrangement of groups of interacting magnetic clusters,[34] rather than with platelet clusters.

The effect of an applied field in increasing H_{hf} can be understood in terms of the proposed model involving superparamagnetism with weak interaction between the magnetic clusters. As discussed above, the field of several kilooersteds induces an appreciable degree of time-averaged alignment of the large cluster moments and restrains the rate of their thermal reorientations. This results in an increased time-average hyperfine field over periods of 10^{-7} seconds acting on the ^{57}Fe nuclei. The same effect can also lead to sufficiently large H_{hf} values for observable hyperfine splitting to take place at higher temperatures, where it is not observable without an applied field, and thus to an increase of T_M. Estimated from $H\mu = k\Delta T$, the magnitude of the cluster moment required to allow a field of 20 kOe to increase T_M from ~ 145 to an estimated ~ 230 K, as in Fig. 3, is $\sim 63\mu_B$. This value may be compared with $\mu \approx 27-39\mu_B$ for quenched $Au_{83}Fe_{17}$ in the same temperature range, estimated by interpolation between the values determined by least-squares fitting for $Au_{85}Fe_{15}$ (Ref. 14) and for $Au_{82}Fe_{18}$.[12] The agreement would be presumably improved if the ferromagnetic interaction between the clusters could be taken into consideration, since this tends to increase the time-average alignment of the cluster moments by the applied field, so that a moment value lower than $63\mu_B$ would suffice for increasing T_M from ~ 145 to ~ 230 K.

The gradual increase of H_{hf} with decreasing temperature between T_M and ~ 50 K as shown for instance by the $H = 0$ curve in Fig. 3, can be attributed to the decreasing rates of thermal reorientation of the cluster moments with decreasing temperatures. The extra increase of H_{hf}, starting at ~ 50 K in the absence of an external field (see Fig. 3), is simply explained in terms of the proposed model as due to the constraints the local anisotropy imposes on the thermal reorientations of the cluster moments, in addition to the effect of cooling just mentioned. The fact that the extra increase of H_{hf} starting at ~ 50 K is absent when an external field of $H = 20$ kOe is applied, as shown by the data of Brand, Manns, and Keune, Fig. 3, is a result of the comparable increase of H_{hf} up to much higher temperatures due to the applied field, as discussed in the previous paragraph. Under such conditions the cluster moments may nearly stand still for periods of $\sim 10^{-7}$ sec at 50 K and at still lower temperatures, so that additional restraint by local anisotropy at those temperatures will have no additional effect on the time-average hyperfine field within the limit of accuracy of the measurement.

It should be noted that the experimental results derived from the Mössbauer spectra can be explained qualitatively on the basis of a model involving essentially superparamagnetic behavior, i.e., only finite magnetic clusters. If an infinite cluster would also be present, one would expect to see a large increase in H_{hf} within a relatively narrow temperature range near T_c to values noticeably higher than H_{hf} due to the finite clusters and the Curie temperature would not be affected by the applied field of 20 kOe. In fact, the Mössbauer spectra furnish no such indication of long-range ferromagnetism of infinite clusters for the alloys with up to 0.19 Fe. But they are entirely compatible with the proposed "superparamagnetic" model with quasirandom local anisotropy thermally overcome at ~ 50 K.

The magnetic specific-heat component having a maximum at ~ 50 K for the gold-iron alloys with 0.15, 0.18, and 0.23 Fe in Fig. 1 of Ref. 18 is quite likely associated with the thermal liberation of the cluster moments from the restraints of the local anisotropy. The areas under the various curves in Fig. 2 of Ref. 18 represent the corresponding entropy changes. Because of extensive overlap of the temperature ranges of the process giving rise to the magnetic specific-heat maximum at ~ 50 K and of the other one associated with the maximum at ~ 170 K for the 0.18 Fe alloy, only a rough order of magnitude estimate of the entropy change is possible. The entropy change due to the ~ 50 K process, estimated from Fig. 2 of Ref. 18 is $\Delta\eta \approx \int (C_m/T)dT \approx 0.3$ joule/mol deg (C_m is the estimated magnetic specific heat due to the 50 K process). A simplistic order of magnitude estimate of the entropy change expected from the thermal liberation of N magnetic cluster moments of magnitude $\mu = gS \approx 160\mu_B$ (from Fig. 2) is $\Delta\eta \approx kN \ln(2S+1) \approx 0.13$ joule/mol deg. Thus, consistently with the proposed interpretation, the entropy change due to the thermal liberation of the cluster moments from the local anisotropy is in order of magnitude agreement with the entropy change estimated for the ~ 50-K process identified by the magnetic specific-heat data.[18]

An interesting feature of magnetic specific-heat data, shown very clearly in Fig. 2 of Ref. 18, is that the temperature of the maximum in the vicinity of 50 K remains essentially constant on increasing the Fe content from 0.15 to 0.23. This proves that the process connected with the ~ 50-K specific-heat maximum is not the "magnetic phase change" at T_F. The temperature of the latter is shown in Ref. 10 to decrease with increasing Fe content to near 0 K at 0.23 Fe. On the other hand, a recent perturbed angular correlation study[35] indicates that the temperature of the onset of the extra increase of H_{hf} over the values extrapolated from higher temperatures is ~ 50 K for $Au_{74}Fe_{26}$, i.e., the same temperature as was found by Mössbauer spectroscopy for this extra increase (and for the onset of temperature-dependent polarization) in alloys with 0.168 Fe,[26] see Fig. 3, and with 0.19 Fe.[27] The constant temperature of ~ 50 K for these changes in the hy-

perfine field independently of the Fe content, at least up to 0.26 Fe, correlates very well indeed with the temperature of the magnetic specific-heat maximum discussed. This correlation is consistent with the interpretation of the magnetic specific-heat maximum given above in terms of the thermal liberation of the individual cluster moments from the constraint of local anisotropy, not involving cooperative effects.

In view of the above considerations, one may predict that quenched $Au_{77}Fe_{23}$ will be also found to show decreasing polarization in its Mössbauer spectrum as well as an extra increase of H_{hf} (in the absence of an external field) with decreasing temperature below ~ 50 K, as do the alloys with 0.17 and 0.19 Fe. Because of the extra increase of H_{hf}, starting at ~ 50 K, indicated by the perturbed angular correlation results[35] for $Au_{74}Fe_{26}$, one can expect this alloy as well to have a magnetic specific-heat component with a maximum at ~ 50 K. Since all these effects in the Mössbauer spectra and in the magnetic specific-heat result from the action of quasirandom local anisotropy on magnetic cluster moments, it appears from the indications available at present that even the alloy with 0.26 Fe may be essentially superparamagnetic, rather than ferromagnetic, despite the doubtless strongly increasing ferromagnetic interaction between the cluster moments in this composition range.

SUMMARY

Magnetization versus field isotherms for $Au_{82}Fe_{18}$ are quantitatively described by a model involving superparamagnetism with interaction between the cluster moments. There is no need for the assumption of long-range ferromagnetism or "infinite clusters." Low-field susceptibility measurements indicate no "magnetic phase transitions," but show a large magneto-thermal-history effect in the entire temperature range where the external susceptibility is largely demagnetization controlled and where the remanence is essentially zero. The magnetic specific-heat data are consistent with the proposed model. Analysis of the magnetization data for quenched $Au_{82}Fe_{18}$ shows the formation of magnetic clusters with large moments at temperatures (e.g., ~ 200 K) well above the onset of demagnetization control of the external susceptibility in a spherical specimen (~ 150 K) and a gradual increase of the cluster moments with decreasing temperature. Remanence becomes observable in quenched $Au_{82}Fe_{18}$ only below 65 K. Below ~ 50 K the polarization due to an applied field, as shown by the Mössbauer spectra for $Au_{83.2}Fe_{16.8}$ and for $Au_{81}Fe_{19}$, decreases with decreasing temperature, while the hyperfine field shows an extra increase (in the absence of an external field). A field of 20 kOe applied to the $Au_{83.2}Fe_{16.8}$ specimen increases the hyperfine field above ~ 20 K and it increases also the temperature where the hyperfine splitting disappears in the Mössbauer spectrum from ~ 140 K to over 200 K. In the presence of this external field there is no perceptible extra increase in the hyperfine field below ~ 50 K. All these effects are explained qualitatively in terms of the proposed model, which assumes that a quasirandom local anisotropy restricts the thermal reorientations of the cluster moments, but that this restriction is removed by thermal activation above ~ 50 K. The component of the magnetic specific heat with a maximum at ~ 50 K for the alloys with 0.15, 0.18, and 0.23 atomic fraction Fe apparently results from the thermal liberation of the cluster moments from the restraints of the local anisotropy. Recent perturbed angular correlation results suggest that even an alloy with as high an Fe content as 0.26 atomic fraction may have a magnetic structure corresponding to the proposed model.

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