Spin glassiness, ferromagnetism, and their coexistence in a Au-Fe alloy

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Magnetization measurements were made on the alloy $Au_{85}Fe_{15}$ quenched from two different annealing temperatures ($T_A = 275$ and 200 °C). In both conditions, the alloy is ferromagnetic from T_c (~ 95 and ~ 105 K, respectively) down to $T_{fg} \approx 30$ K, where it transforms to a reentrant spin-glass-like state, as evidenced by its irreversible time-dependent magnetic properties. However, the time-independent magnetizations (M) measured in various fixed fields applied during cooling ($H_{\rm cool}$) reveal a significant thermodynamic difference between the reentrant states in the two cases. For $T_A = 275$ °C, the $M(H_{\rm cool})$ isotherms below T_{fg} have a finite initial slope, as in a normal spin glass, whereas for $T_A = 200$ °C, the corresponding isotherms exhibit a spontaneous ferromagnetic moment, indicating that the state is mixed. In the magnetic phase diagram with T_A^{-1} as abscissa, the boundary line between the mixed and nonmixed spin-glass-like states lies well away from the multicritical point, in apparent disagreement with theoretical expectation. The magnetization behavior near T_{fg} suggests that the transition from reentrant state to ferromagnetism is continuous and that some spin-glass order persists into the ferromagnetic state.

INTRODUCTION

Of the numerous disordered magnetic systems that exhibit properties characteristic of a spin glass (SG), many are now known to have regimes of chemical composition where these properties appear at a temperature below the Curie point of a ferromagnetic (FM) state.[1] Typically, as a function of composition, the temperature (T_{fg}) for the onset of this so-called "reentrant" SG state is seen to rise and meet the descending FM Curie temperature (T_c) at a multicritical point (mcp), beyond which there is a single transition temperature (T_g) marking the direct disordering (or unfreezing) of the SG state. This type of magnetic phase diagram has been predicted theoretically for a system whose exchange-field distribution manifests a competition between SG and FM ordering.[2] Moreover, although the SG state on both sides of the mcp displays similar characteristic properties (e.g., a time-dependent remanent magnetization after field cooling), more recent theoretical work has predicted that as a reentrant state it should also exhibit a spontaneous FM moment at equilibrium; it was therefore referred to as a "mixed" state.[3] Very recent measurements on disordered Ni-Mn have revealed that the reentrant state of the alloy $Ni_{77}Mn_{23}$ is indeed mixed, in that the time-independent magnetizations (M) measured in various fixed fields applied during cooling ($H_{\rm cool}$) describe isothermal $M(H_{\rm cool})$ curves that (after demagnetization correction) rise abruptly to nonzero spontaneous values—whereas for the alloy $Ni_{75}Mn_{25}$, which is just on the other side of the mcp, the corresponding $M(H_{\rm cool})$ curves rise rapidly but with finite initial slopes.[4]

It has therefore become of experimental interest to learn if the reentrant state in systems other than Ni-Mn shows an analogously mixed behavior. For this purpose, we chose to investigate Au-Fe which, at sufficiently high Fe concentrations ($\gtrsim 14$ at. %), departs from its simple SG regime and enters via a mcp into a FM regime with a reentrant SG-like state at lower temperatures.[5,6] Even at these compositions, Au-Fe alloys are readily retained in the fcc-structured phase by quenching from high temperatures, though subsequent annealing at lower temperatures produces various degrees of short-range atomic clustering (i.e., antiordering).[7] In fact, it was recently demonstrated that progressive lowering of the annealing temperature for alloys of 14 and 15 at. % Fe results in changes of magnetic state that resemble those seen (as described above) in identically treated alloys of increasing Fe concentration.[8] Since this annealing approach has experimental advantages, we decided to use it in a detailed magnetization study of the alloy $Au_{85}Fe_{15}$ in different metallurgical conditions. The results of this study are presented here and show that the reentrant state of this alloy does indeed have a mixed FM-SG nature but only well away from the multicritical point. Moreover, the ferromagnetic state itself appears to indicate a coexistent spin-glass ordering.

RESULTS AND COMMENTARY

The alloy sample we have investigated is the small (~ 0.14 g) rod-shaped sample of $Au_{85}Fe_{15}$, cut from an arc-melted button, that had recently been studied magnetically after an initial homogenization anneal at 950 °C followed by treatments at various lower temperatures.[8] This previous study had determined the magnetic phase diagram reproduced in Fig. 1, where various transition temperatures are plotted (as open symbols) versus the inverse of the annealing temperature (T_A) from which the sample had been rapidly quenched. It was assumed, based on earlier work on similar alloys,[9] that T_A^{-1} is a proportional measure of the degree of atomic clustering, a parameter to be considered roughly comparable to the Fe concentration of a disordered alloy. We note that the line of FM Curie

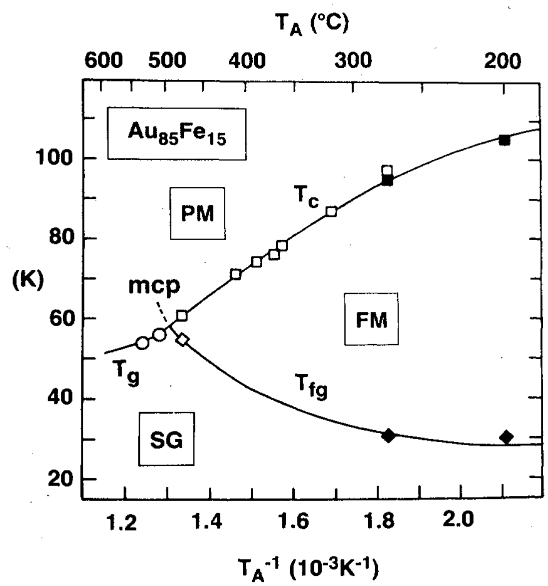

FIG. 1. Magnetic phase diagram of $Au_{85}Fe_{15}$ as a function of T_A^{-1} (where T_A is sample annealing temperature) showing spin-glass (SG), ferromagnetic (FM), and paramagnetic (PM) regimes. Open and closed symbols represent transition temperatures reported in Ref. 8 and in the present paper, respectively.

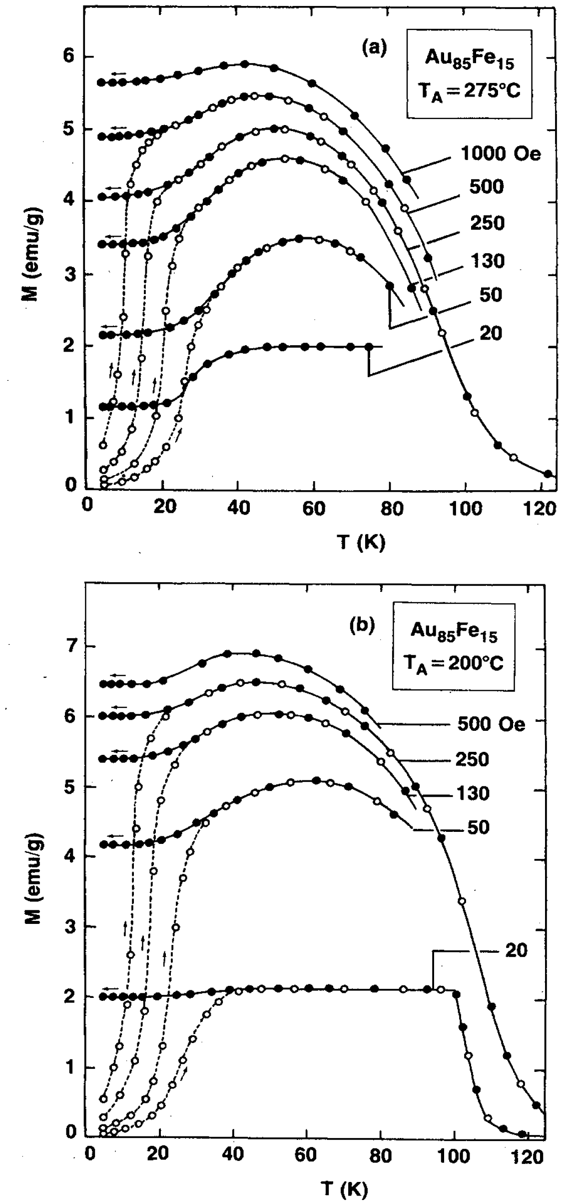

FIG. 2. Magnetization versus temperature at various applied fields for $Au_{85}Fe_{15}$ annealed (a) at 275 °C and (b) at 200 °C. Open and closed circles represent measurements made with increasing and decreasing temperature, respectively, at constant applied fields, after initial zero-field cooling to 4.2 K.

points (T_c), the line of SG freezing temperatures (T_g), and a line based on one point marking a reentrant temperature (T_{fg}) are all meeting at a multicritical point located at $T_A \approx 500\,°C$. The closed-symbol points added to this figure represent our present results and will be discussed later.

Our study of $Au_{85}Fe_{15}$ began with the sample water-quenched after a one-day anneal at $T_A = 275\,°C$ (following a short disordering anneal at 700 °C); to prevent any further changes, the sample was always kept in liquid nitrogen between experiments. The sample was cooled to 4.2 K in zero field and its magnetizations (M) were then measured in a Foner magnetometer as it was slowly warmed up to ~ 80 K and cooled back to 4.2 K in a constant applied field (H_a). This procedure was repeated for different values of H_a, and the results for M as a function of temperature (T) are displayed in Fig. 2(a). For each H_a, the initial value of M at 4.2 K is very low, but as T is raised to a threshold value (which decreases with increasing H_a) M rises extremely rapidly and then continues to change gradually. Upon subsequent cooling in the same fixed H_a, M retraces the gradual part of its trajectory but then, instead of dropping rapidly, it levels out at a relatively high value.

Thus, there is an enormous magnetic irreversibility, which extends up to ~ 30 K at 50 Oe but to lower T at higher H_a. Furthermore, in this region of irreversibility, the magnetizations measured with increasing temperature (represented by the dashed curves in the figure) were seen to rise slowly and steadily with time, whereas at higher temperatures and upon subsequent cooling to 4.2 K, the magnetizations (represented by the solid curves) showed no detectable time dependence. Irreversibilities of this kind, accompanied by such differences in time dependence between the field-cooled and zero-field-cooled magnetizations, are commonly regarded as signatures of a spin-glass state.[10]

In the reversible region at higher temperatures, despite the peculiar shapes of the M-versus-T curves, the alloy $Au_{85}Fe_{15}$ passes through a ferromagnetic state, as evidenced in Fig. 2(a) by its demagnetization-limited values of M at 20 Oe above ~ 50 K. To check the existence of a spontaneous moment at these and lower temperatures, we followed the solid time-independent M-versus-T curves down to 4.2 K and plotted these (and additional) data as isotherms of M versus H_{cool}, the constant field applied during cooling. These are shown in Fig. 3(a). We note at 50 K that there is a gradual high-field approach to saturation and that M at low $H_{\rm cool}$ merges into the demagnetization curve for the sample (labeled D) at a spontaneous magnetization ($M_{\rm sp}$) value of ~ 2 emu/g. At 35 K, the $M(H_{\rm cool})$ behavior is very similar but with $M_{\rm sp}$ somewhat lower (~ 1.5 emu/g). However, at 20 and 4.2 K, although the $M(H_{\rm cool})$ curves continue to show a gradual high-field saturation effect, they descend all the way to the origin before meeting the D curve, thereby indicating that $M_{\rm sp}$ has gone to zero. Thus, in this metallurgical condition (i.e., for $T_A = 275\,^{\circ}\mathrm{C}$), the alloy has a reentrant state whose time-independent field-cooled properties resemble those of a simple spin glass, showing no evidence of any mixed character. At $T_{fg} \approx 30$ K, the alloy does become ferromagnetic and remains so up to $T_c \approx 95$ K, as estimated from the inflection point of the $M(T)$ curve for 250 Oe in Fig. 2(a).

To investigate any qualitative changes that may occur when the alloy $Au_{85}Fe_{15}$ is removed further from the multicritical point, we later annealed the sample for one day at $T_A = 200\,^{\circ}\mathrm{C}$ and quenched it from this lower temperature, thus increasing the degree of atomic clustering. The same measurements of M versus T at various fixed values of H_a were repeated, and the results are shown in Fig. 2(b). Again, the magnetization exhibits a pronounced irreversibility over approximately the same temperature range, i.e., up to ~ 30 K at $H_a = 50$ Oe, with the values of M measured during field cooling being time independent. This behavior again signifies a reentrant SG-like state below $T_{fg} \approx 30$ K, and the ferromagnetic state now extends up to $T_c \approx 105$ K, as evidenced by the inflection point of the 250-Oe curve as well as by the sharp kink in the curve for 20 Oe. The latter curve is demagnetization limited and remains so upon field cooling all the way down to 4.2 K, in contrast to the 20-Oe curve in Fig. 2(a). These and additional data are plotted as $M(H_{\rm cool})$ isotherms in Fig. 3(b), and it is seen that these curves are considerably different from those in Fig. 3(a). The curves for 50 and 35 K show a more rapid approach to saturation, and at low $H_{\rm cool}$ they merge with the D curve at higher values of $M_{\rm sp}$ (~ 4.5 and ~ 4 emu/g, respectively). But more significantly, the curves for 20 and 4.2 K indicate that now $M_{\rm sp}$ does not vanish at these temperatures but remains essentially constant at ~ 3 emu/g. Thus, the reentrant state of the alloy for $T_A = 200\,^{\circ}\mathrm{C}$ has a nonzero FM moment and, since it also exhibits SG-like properties,

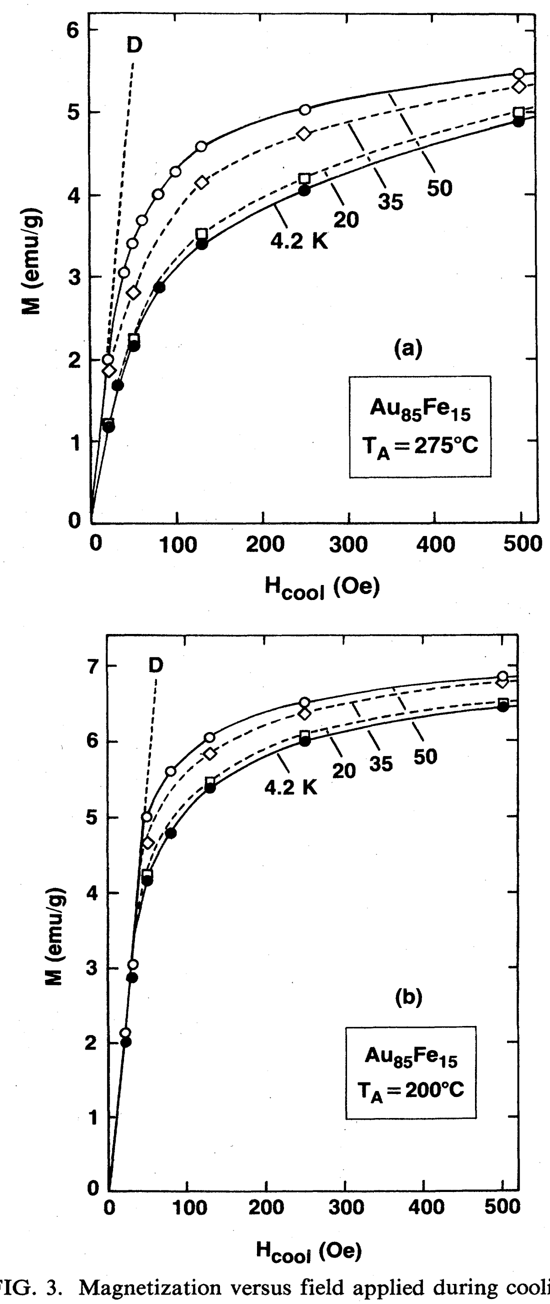

FIG. 3. Magnetization versus field applied during cooling to various temperatures for $Au_{85}Fe_{15}$ annealed (a) at 275 °C and (b) at 200 °C. Dotted line (D) represents demagnetization.

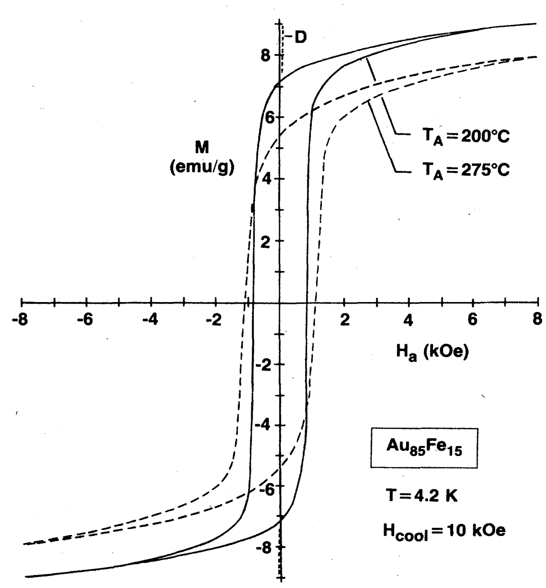

FIG. 4. Magnetic hysteresis loops measured after cooling to 4.2 K in 10-kOe field, for $Au_{85}Fe_{15}$ annealed at 200 °C (solid curves) and at 275 °C (dashed curves). Demagnetization shown by dotted line (D).

it conforms to the operational description of a mixed state.

To elucidate further the reentrant states for these two metallurgical conditions of the alloy, some additional experiments were performed, involving the hysteretic behavior after field cooling. In both cases, the sample was initially cooled from ~80 down to 4.2 K in a 10-kOe field. Complete hysteresis loops were then measured over the field range of ±8 kOe, and these are displayed in Fig. 4. Both loops are wide and symmetrical about the origin, as opposed to the narrow displaced loops typically seen in the SG alloys containing Mn after similar field cooling.[4,11,12] Although the loop for $T_A=200\,°\mathrm{C}$ has a smaller coercive field (H_c), its remanent magnetization (M_R) is larger, such that its area is about the same as that of the loop for $T_A=275\,°\mathrm{C}$. The main qualitative difference between them is that the loop for $T_A=200\,°\mathrm{C}$, after correction for demagnetization (D curve shown dotted), is vertical as it passes through the field axis, which presumably reflects the mixed FM-SG nature of the reentrant state for this condition of the alloy.

Subsequently, in both cases of T_A, the hysteresis-loop measurements were repeated at various temperatures as the sample was slowly warmed up. The results are represented by the values of M_R and H_c plotted versus T in Fig. 5. The variation of H_c is similar in the two cases, showing a monotonic decrease with increasing T, which is rapid at first but slows down as H_c approaches the T axis tangentially and merges with it at or near $T_{fg}\approx 30$ K. The corresponding decrease of M_R appears to be linear in both cases but with a telltale difference. For $T_A=275\,°\mathrm{C}$, the linear decrease extends all the way down to zero M_R

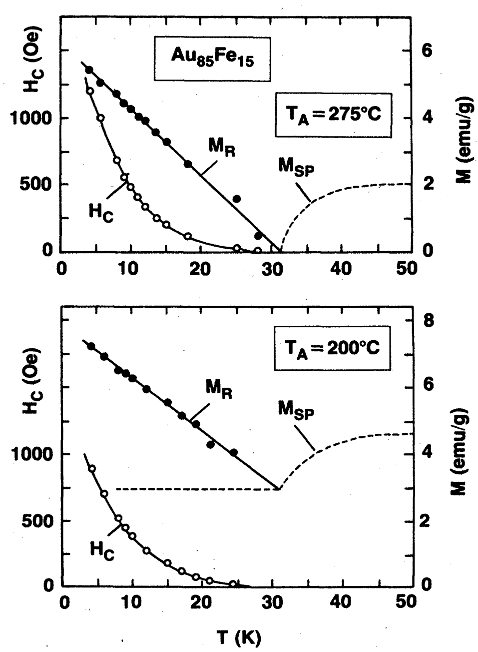

FIG. 5. Remanent magnetization (M_R) and coercive field (H_c) from hysteresis loops at various temperatures, for $Au_{85}Fe_{15}$ annealed (a) at 275 °C and (b) at 200 °C. Dashed curves represent spontaneous magnetization (M_{sp}).

as T reaches T_{fg}, whereas for $T_A=200\,°\mathrm{C}$, M_R heads linearly into the value of M_{sp} (~3 emu/g) that prevails at and below T_{fg}. Thus these results not only describe the hysteretic behavior of the reentrant state but also provide corroborating evidence that the spontaneous FM moment associated with this state is zero or nonzero, depending on the metallurgical condition of the alloy.

SUMMARY AND DISCUSSION

Our results have shown that after annealing treatments at $T_A=275$ and 200 °C, the alloy $Au_{85}Fe_{15}$ is ferromagnetic with Curie temperatures (T_c) of ~95 and ~105 K, respectively, and transforms upon cooling through $T_{fg}\approx 30$ K to a reentrant state. Plotted in Fig. 1, these transition temperatures give reasonable extensions to the magnetic phase diagram that was previously determined for this alloy as a function of T_A.[8] In both cases of T_A investigated here, the reentrant state is observed to have irreversible and time-dependent magnetic properties which testify to its spin-glass-like nature. Moreover, in the case of $T_A=275\,°\mathrm{C}$, the time-independent magnetizations measured during cooling in various fixed fields indicate the absence of any spontaneous ferromagnetic moment in the reentrant state at equilibrium. But in the case of $T_A=200\,°\mathrm{C}$, similar measurements reveal that the reentrant state is indeed characterized by a nonzero ferromagnetic moment, which is indicative of the mixed state predicted by Gabay and Toulouse[3] and recently observed in Ni-Mn.[4] However, for our Au-Fe alloy sample, the boundary line separating the mixed state from the simple spin-glass state lies well away from the multicritical point, whereas the theoretical prediction has it descending vertically from the mcp,[3] but this matter needs to be investigated further as a function of Au-Fe composition.

The smooth variations of the spontaneous magnetization M_{sp} with temperature near T_{fg}, as depicted in Fig. 5, indicate that the transitions from ferromagnetism to the reentrant state are continuous in the cases we have studied. Moreover, the gradualness of these transitions, which is reflected in the anomalously peaked shapes of the M-versus-T curves in Fig. 2, suggests that the ferromagnetic state has an increasing amount of coexistent spin-glass order as the temperature decreases towards T_{fg}. It is pertinent to note here that the magnetizations measured at these temperatures, even in moderately high fields, are considerably lower than the value of 10.5 emu/g that would result from the parallel alignment of all the Fe atomic moments [of magnitude $2.2\mu_B$ (Ref. 13)] in the alloy. Another peculiar but probably related feature of the ferromagnetic state of $Au_{85}Fe_{15}$ is the extremely high (if not infinite) rate at which the magnetization rises with increasing field from its spontaneous value, as seen in Fig. 3. This enormous initial differential susceptibility continues into the reentrant state when it is mixed (i.e., in the case of $T_A=200\,°\mathrm{C}$), and this was also recently observed in the alloy $Ni_{77}Mn_{23}$.[4] Thus, it would appear that due to a persistent frustration many of the spins (of individual atoms and/or clusters) are weakly coupled into randomly aligned configurations that are readily affected by small external fields—such that the ferromagnetic state itself (especially just above T_{fg}) has a mixed character. A similar conclusion was recently reached from Mössbauer measurements on the alloy $Au_{81}Fe_{19}$, for which it was claimed that the ferromagnetic state well below T_c involved spin configurations with "random local canting."[14] For the same $Au_{81}Fe_{19}$ alloy, incidentally, the hysteresis-loop behavior of the reentrant state was very recently studied for various field-cooling treatments, but no results were reported for the time-independent magnetizations to be seen in the fixed fields applied during cooling.[15]

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[1]For some very recent reports on spin-glass reentrant phenomena, see pp. 1673—1708, the relevant section of the *Proceedings of the 1983 Conference on Magnetism and Magnetic Materials* [J. Appl. Phys. **55**, 1623 (1984)]. For earlier experimental work, see the references cited in Ref. 4.

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