Magnetic phase diagram of disordered Ni-Mn near the multicritical point

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From detailed magnetization data taken under various field-cooling conditions, the magnetic phase diagram of temperature versus composition is determined for disordered Ni-Mn of Mn concentration (x) near 25 at. %. With increasing x, the ferromagnetic Curie-point (T_c) line descends and meets the ascending line for the spin-glass reentrance temperature (T_{fg}) at a multicritical point (MCP) located at $x=23.9$, $T=102$ K, from which the spin-glass freezing-temperature (T_g) line emerges and reaches a maximum at higher x. The reentrant spin-glass (SG) ordering is accompanied by a net ferromagnetic (FM) moment, thus describing a mixed ferro-spin-glass (FSG) state, which is separated from the normal SG state by a boundary line that extends essentially vertically down in temperature from the MCP. Moreover, it is shown that the SG ordering of the FSG state probably persists into the FM regime above T_{fg}, where T_{fg} (like T_g) remains defined operationally by the appearance of irreversible and time-dependent magnetic effects.

INTRODUCTION

Among the numerous chemically disordered (crystalline or amorphous) magnetic systems that exhibit spin-glass (SG) properties, many are known to become ferromagnetic (FM) at a critical composition, beyond which the SG state continues to appear at some temperature (T_{fg}) progressively lower than the FM Curie point (T_c). The SG state is then commonly referred to as "reentrant."[1] Typically, the critical composition locates a multicritical point (MCP) at which T_{fg} and T_c come together and on the other side of which there is a single transition temperature (T_g) marking a freezing out of the "normal" SG state directly from the paramagnetic state. Such a magnetic phase diagram has been predicted theoretically[2] for a model system in which there is a composition-dependent FM bias to the conflicting (thus frustrated) demands of the exchange interactions among the randomly situated magnetic atoms. From similar considerations, it was later predicted that the normal and reentrant SG states are distinct, in that the latter has a spontaneous FM moment coexistent with the SG ordering and therefore can be called "mixed."[3] However, until fairly recently, there had been no reported magnetization evidence for this phenomenon.

From a detailed magnetic study of several disordered Ni-Mn alloys,[4] we recently confirmed the previously reported[5] occurrence of a reentrant SG state and found that the MCP lies somewhere between 23 and 25 at. % Mn. This study also revealed that the reentrant SG state of $Ni_{77}Mn_{23}$, though similar to the normal SG state of $Ni_{75}Mn_{25}$ in the time-dependent displaced hysteresis loops exhibited after field-cooling, differs markedly in the time-independent magnetizations (M) measured in different steady fields (H_{cool}) applied during cooling. The low-temperature $M(H_{cool})$ curve for $Ni_{77}Mn_{23}$ (when corrected for demagnetization) shows unambiguously a nonzero value for the spontaneous magnetization, whereas the corresponding (corrected) curve for $Ni_{75}Mn_{25}$ emerges from the origin with a large but finite slope. Allowing that these two alloy compositions are not very close, our results implied that in the temperature-versus-composition phase diagram the boundary line between the mixed and normal SG states extends down fairly vertically from the MCP. This is in tentative agreement with the prediction of Gabay and Toulouse[3] but contrasts with the results of a similar study of Au-Fe,[6] which place the descent of this boundary line well away from (on the FM side of) the MCP.

A more detailed and complete magnetic phase diagram for disordered Ni-Mn near the MCP is clearly needed. It would provide a firmer framework for any improved understanding of reentrant SG systems in general and of the diverse magnetic properties of the Ni-Mn system in particular. In this paper, we present experimental results leading to the determination of such a phase diagram, including closer evidence regarding the location of the boundary line between the mixed and normal SG phases. And in the following paper,[7] this magnetic phase diagram serves as an essential reference for the changes with composition of various measured properties and of the corresponding parameters of a ferro-spin-glass domain model for Ni-Mn.

EXPERIMENTAL RESULTS AND DISCUSSION

To supplement the Ni-Mn alloy samples of 23, 25, and 27 at. % Mn that we had studied earlier,[4] we arc-melted together (under argon) appropriate proportions of the ingots of these alloys to form new alloy ingots of 23.5, 24, 24.5, and 26 at. % Mn. After the ingots were homogenized for 3 days at 900 °C, a small rectangular rod sample ($\sim 7\times 1.5\times 1.5$ mm^3) was spark cut from each and its sharp corners rounded off in order that the demagnetization be reasonably uniform. Each sample, old and new, was quartz encapsulated in argon, annealed for 2 h at 900 °C, and quenched into water. This treatment ensured the absence of the ordered Ni_3Mn phase, which is strongly ferromagnetic ($T_c \approx 700$ K), but probably did not prevent some atomic short-range order (of about the same amount in the different samples). To avoid any additional short-range ordering, the samples were stored in liquid nitrogen when not in use. Their magnetizations were measured with a vibrating-sample magnetometer at temperatures down to 4.2 K in fields applied along the sample rod axis.

In the initial experiments, each Ni-Mn sample was first cooled to 4.2 K in zero field. A small field (H_a) was then applied and held constant while the sample temperature (T) was raised slowly up to ~ 200 K and subsequently lowered slowly back to 4.2 K. During this temperature cycle, the sample magnetization (M) was measured quasistatically at intervals of ~ 5 K. The results are displayed in Fig. 1. For the alloys of Mn concentration $x \geqq 24$ at. %, we see that M for increasing T (solid curves) passes through a maximum, whereas for decreasing T (dashed curves) M continues to rise beyond the maximum and gradually levels off. This irreversibility with temperature is quite typical of a spin glass, although in other systems [e.g., Cu-Mn (Ref. 8)] the decreasing-T curve drops slightly before leveling off. Also typical is the fact that in the region of irreversibility the increasing-T curve varies with time (with M slowly rising isothermally) but the decreasing-T curve is essentially time-independent, as are both curves in the reversible region at higher temperatures. In all cases the two curves separate tangentially at a temperature just above that of the increasing-T maximum, and following standard practice we define this temperature as the SG freezing point (T_g).

For the alloys of $x = 23$ and 23.5, the curves in Fig. 1 show a similar low-temperature region of irreversibility but are qualitatively different in the reversible region, where at temperatures up to a kink point M remains constant at the demagnetization-limited value of H_a/D, D being the demagnetization factor of the samples (~ 4.5 Oe g/emu). This behavior signals the occurrence of ferromagnetism and the kink-point temperature extrapolated to zero H_a (as shown dotted) gives T_c. The temperature at which the increasing-T and decreasing-T curves separate is now labeled T_{fg}. Below T_{fg} the latter curves rise to slightly above the H_a/D value, implying the existence of magnetic hysteresis in the reentrant SG state.

As a measure of the approach to ferromagnetism with decreasing x (at. % Mn), the ratio χ_m/χ_0 and its reciprocal are plotted against x in Fig. 2, where χ_m and χ_0 are the demagnetization-corrected low-field susceptibilities at the maximum and at 4.2 K after zero-field-cooling, respectively. At $x = 27$, $\chi_m/\chi_0 \approx 3.9$, which is fairly typical of a normal spin glass, but as x decreases χ_m/χ_0 rises at an increasing rate and reaches a very large value (~ 37) at $x = 24$, thus anticipating the onset of ferromagnetism at slightly lower x. Indeed, the reciprocal ratio χ_0/χ_m shows an essentially linear decrease that extrapolates to zero at $x \approx 23.9$, below which it remains zero, as exemplified by the ferromagnetic (and reentrant) alloys of $x = 23.5$ and 23.

In the magnetic phase diagram of Fig. 3, the values of the various transition temperatures (T_g, T_{fg}, T_c) taken from Fig. 1 are plotted against alloy composition. Note that the increase of T_{fg} with increasing x (at. % Mn) joins continuously with the increase of T_g. The latter then proceeds to reach a maximum at $x \approx 24.7$ and to decrease slowly at higher x. Such a nonmonotonic variation of T_g near the MCP is not typical. (Interestingly, at x between 30 and 35 long-range antiferromagnetism sets in, according to recent neutron diffraction work[9]). As Fig. 3 also shows, the decrease of T_c with increasing x is based on

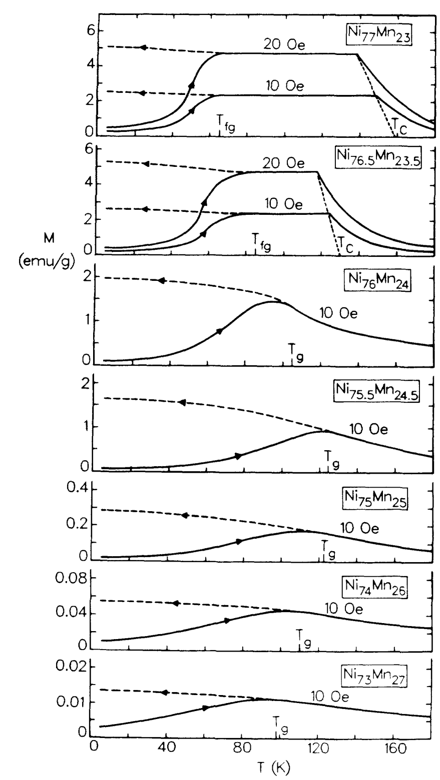

FIG. 1. Magnetization versus temperature for various Ni-Mn alloys, initially zero-field cooled to 4.2 K, upon warming (solid curves) and then cooling (dashed curves) in a constant magnetic field.

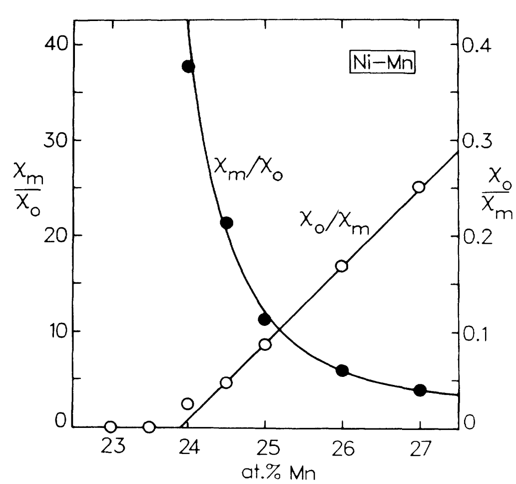

FIG. 2. χ_m/χ_0 and its reciprocal versus at. % Mn in Ni-Mn, where χ_m and χ_0 are the low-field (demagnetization-corrected) susceptibilities at their maximum values and at 4.2 K, respectively, after zero-field cooling.

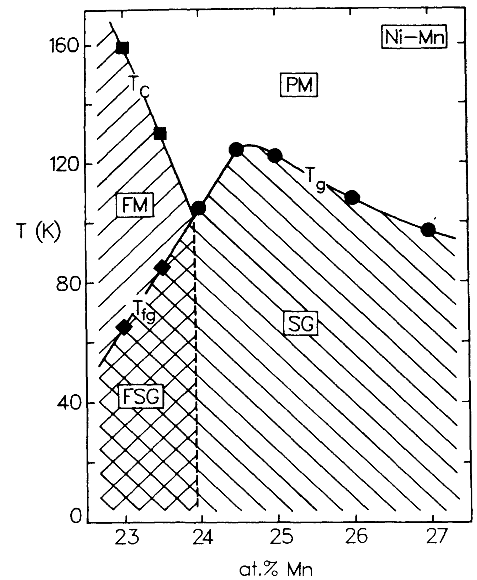

FIG. 3. Magnetic phase diagram of temperature versus composition for disordered Ni-Mn, showing ferromagnetic (FM), reentrant, ferro-spin-glass (FSG), normal spin-glass (SG), and paramagnetic (PM) regimes. The T_c, T_{fg}, and T_g lines (and the vertical line between FSG and SG) all meet at a multicritical point (23.9 at. % Mn, 102 K). The FM state probably contains some SG order, as discussed in the text.

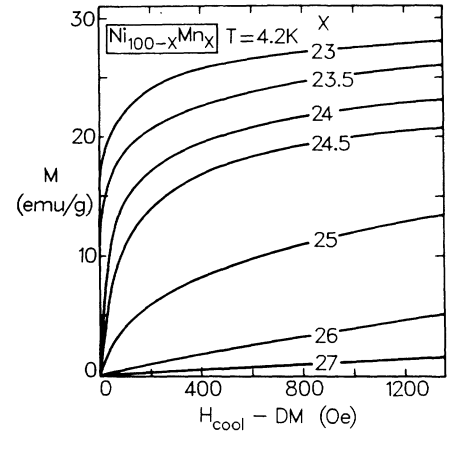

FIG. 4. Magnetization measured at 4.2 K in the field applied during cooling (H_{cool}) plotted versus the demagnetization-corrected H_{cool}, for Ni-Mn of various at. % Mn.

two points (at $x=23$ and 23.5) but they suffice for the purpose since the line drawn through them must extend to the left of the T_g point at $x=24$. The T_c line was therefore given a mild concave-downward curvature so as to meet the $T_{fg}-T_g$ line at $x=23.9$, the x value at which χ_m/χ_0 displays a divergence (Fig. 2). The meeting of these lines at $x=23.9$ and $T=102$ K represents the location of the multicritical point.

As described earlier, the boundary line between the mixed ferro-spin-glass (FSG) phase and the normal SG phase was shown by our previous work[4] to lie between $x=23$ and 25. To locate this boundary line more precisely with respect to the MCP, similar measurements were performed on our new alloy samples. Specifically, we cooled each sample slowly from above T_{fg} or T_g down to 4.2 K in a constant field (H_{cool}) and measured its time-independent magnetization (M) in this field. Repeating this procedure for different H_{cool}, we obtained a locus of $M(H_{cool})$ points pertinent to 4.2 K. Our demagnetization-corrected results are plotted as curves of M versus $H_{cool}-DM$ in Fig. 4, where our previously determined curves for $x=23$, 25, and 27 are also exhibited. It is clear that as x decreases from 27 to 24 the curves become strikingly nonlinear but continue to emerge from the origin with finite slopes. However, the initial slope is increasing rapidly and appears to be diverging as x approaches a value just under 24, very close to the x value of the MCP. In fact, when x reaches 23.5 the curve merges tangentially with the M axis at ~ 11 emu/g, representing a spontaneous FM moment—and similarly, as reported earlier,[4] the curve for $x=23$ gives a FM moment of ~ 16 emu/g.

This behavior testifies to a definite (probably continuous) transition between the normal SG and mixed FSG states, which at 4.2 K occurs very near (if not precisely at) the multicritical-point composition. Hence, in the phase diagram of Fig. 3, the boundary line between these states is shown as extending vertically down from the MCP, in essential agreement with the prediction of Gabay and Toulouse.[3] According to this prediction, the reentrant state below T_{fg} involves a SG ordering of the spin components transverse to the coexistent FM moment, while in the FM state above T_{fg} the transverse SG order is absent and only the FM alignment of the longitudinal spin components remains. However, although our Ni-Mn results evidence the existence of a FM moment in the reentrant state (as also suggested by recent inelastic neutron scattering work[10]), other aspects of the Gabay-Toulouse picture are not borne out so clearly by our observations.

In particular, we have examined the detailed variation of the spontaneous FM moment (M_{sp}) of the 23- and 23.5-at. % Mn alloys as the temperature decreases from T_c, where M_{sp} was again obtained by extrapolating time-independent $M(H_{cool}-DM)$ curves to $H_{cool}-DM=0$. For each of these reentrant alloys, M_{sp} rises monotonically at a diminishing rate and is gradually leveling off as the temperature is decreasing through T_{fg}; there is not detectable anomaly signaling any onset of SG order. Moreover, the values of M_{sp} for the state just above T_{fg}, which are not much below the M_{sp} values at 4.2 K (~ 16 and ~ 11 emu/g), are substantially lower than the theoretical saturation value of ~ 95 emu/g corresponding to a FM alignment of all the Ni and Mn atomic moments in these alloys.[11] This discrepancy is much too large to be ascribable to thermal effects and thus may be taken as evidence that, coexistent with the ferromagnetism, some SG order persists at temperatures above T_{fg}. Hence, the temperature for the onset of SG ordering (which perhaps identifies the actual Gabay-Toulouse reentrant transition) probably lies significantly higher than the temperature identified as T_{fg} from the appearance of magnetic irreversibility (Fig. 1). A similar distinction between these two temperatures was deduced recently for reentrant Au-Fe on the basis of magnetization,[12] magnetoresistance,[12] and Mössbauer[13] measurements. The intervening state was characterized as "randomly canted ferromagnetism,"[12] which implies a FM-SG coexistence.

However, in Au-Fe the reentrant SG state below T_{fg} exhibits no spontaneous FM moment [except, perhaps, at compositions well removed from the MCP (Ref. 6)], whereas Ni-Mn in its reentrant state is shown here to be consistently a mixed FSG. Consequently, in the case of Ni-Mn, it appears that the only distinction between the states below and just above T_{fg} is the operational one involving the occurrence or nonoccurrence of irreversible (and time-dependent) effects. That the spin configurations of Ni-Mn in these two states may be basically alike has been indicated by resistivity measurements which showed no observable change upon crossing T_{fg}.[14] Based on these and on our subsequent magnetic measurements,[4] it was proposed that the zero-field-cooled state below T_{fg}, whose low-field magnetizations are very low (Fig. 1), consists of FSG domains with net FM moments (and unidirectional anisotropies) that are randomly oriented. The application of this domain picture to Ni-Mn alloys on either side of the multicritical-point composition is explored in the following paper.[7]

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