Structure-sensitive magnetic properties of Ni-Mn alloys

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Quenched Ni-Mn alloys exhibit both a spin-glass state and ferromagnetism for Mn concentrations (c_{Mn}) below 26 at. %. While previous studies concentrated on understanding various aspects of the magnetic properties (hysteresis, field cooling effects, anisotropy, spin waves, etc.), the present study focuses on the effect of structure by sputtering Ni-Mn alloys at temperatures (T_D) ranging from 77 to 1173 K. All magnetic properties (susceptibility, spin-glass transition temperature, and the presence of a displaced hysteresis loop) depend strongly on T_D. Although the lattice parameter tends to increase with increasing T_D, there is no monotonic variation of the magnetic properties with T_D. However, for $C_{\mathrm{Mn}} > 26$ at. % films deposited at 873 K (the order-disorder temperature) show the greatest amount of ferromagnetism and the most pronounced displaced hysteresis loop. On the other hand, films deposited at 77 K (whether amorphous or not) display the most ideal spin-glass behavior without displaced hysteresis loop. This observation, as well as similar behavior reported on crystalline Cu-Mn films, suggests that a displaced hysteresis loop is the result of a specific structure and is not necessarily linked to the spin-glass state.

I. INTRODUCTION

Ni-Mn alloys display interesting magnetic properties and, in particular, $Ni_{78}Mn_{22}$ exhibits coexisting spin-glass and ferromagnetic states.[1] More specifically, a sharp increase in the magnetization at a field of about 150 Oe at temperatures below 40 K was interpreted as a field-induced transition from a spin-glass to a ferromagnetic state[1] and more recently by the presence of anisotropy fields.[2] Furthermore, neutron scattering experiments[3] have revealed well-defined spin waves at all temperatures below the Curie temperature of 330 K and especially below the spin-glass temperature $T_{\mathrm{SG}} = 40$ K which corresponds to the downturn in the susceptibility. The spin-glass state below 40 K was established[1] by both a time-dependent magnetization and a displaced hysteresis loop. In all these studies,[1-3] the samples were prepared in a similar way by annealing at 900—1000 °C followed by water quenching. Although this treatment is supposed to ensure the absence of ordered Ni_3Mn, it is not obvious that it completely prevents short-range atomic order.[1] As a matter of fact, two samples cut from the same $Ni_{74}Mn_{26}$ ingot yielded a small spontaneous magnetization in one sample and not in the other. This discrepancy[1] was attributed to different degrees of short-range order. It is the purpose of this study to examine the effect of structure on the magnetic properties by preparing Ni-Mn alloy films with a wide variety of deposition conditions (rate, film thickness, and T_D).

II. EXPERIMENTAL PROCEDURE

The Ni-Mn sputtering targets were prepared by melting inductively the desired composition in an alumina crucible. The targets were then getter-sputtered onto sapphire substrates at powers ranging from 1 W (1000 V, 1 mA) to 15 W (1500 V, 10 mA). For depositions at room temperature and at 77 K, the substrates were held in a Cu table. For depositions above room temperature, the substrates were held on a Ta table which was heated resistively by passing current between two heavy posts through which liquid nitrogen was circulated during the whole run. At the end of the run, the sputtering power and table current were stopped simultaneously, thus quenching the sample from T_D to 77 K almost instantly by conductive cooling. In the case of deposition at 77 K, the samples could be transferred without warming up above 77 K onto the susceptibility holder. The ac susceptibility of the films was

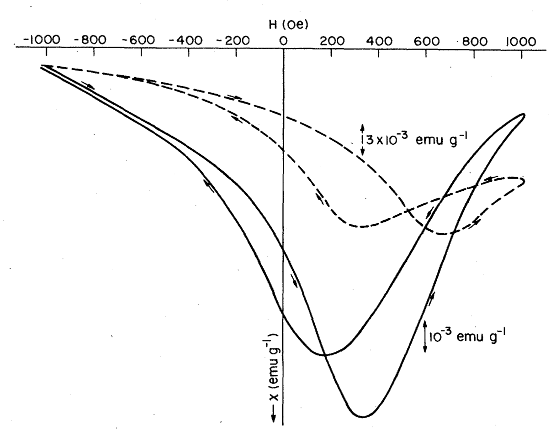

FIG. 1. $\chi_{\mathrm{ac}}(4.2\text{ K})$ as a function of magnetic field after cooling in -250 Oe. The solid curves and solid χ_{ac} scale refer to the 22 at. % Mn target while the dashed curves and dashed χ_{ac} scale pertain to film $Ni_{78}Mn_{22}$ No. 3.

measured at 10 kHz with a modulating field of 4 Oe with a push-rod susceptibility holder.[4] The modulating field is applied in the plane of the film to avoid demagnetization effects. The occurrence of ferromagnetism was established by the presence of a hysteresis loop of χ_{ac} versus a dc magnetic field also applied in the plane of the film. This produces the well-known butterfly curves; an example of such curves as distorted by field-cooling effects is shown in Fig. 1. The film thickness was determined from the weight gain using a linear average of the Ni and Mn densities. The composition of the films and targets was checked by x-ray fluorescence and x-ray diffraction.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Since the magnetic properties of quenched Ni-Mn alloys depend strongly on composition around 26 at. % Mn, it is essential to ensure an accurate composition in both the targets and the films. The properties of Ni-Mn targets are listed in Table I and it is clear that the compositional control is excellent since as shown by the first two columns the lattice parameter (a) increases linearly with c_{Mn}. The magnetic properties of these targets are similar to those reported on quenched alloys.[1] There are, however, important differences which arise, of course, from the different preparation methods. It was not judged necessary to subject the targets to the previously reported treatment[1-3] (annealing at 900–1000 °C followed by water quenching) since the targets are broken up into atoms during the sputtering process and as will be shown in this study, the magnetic properties vary markedly with deposition conditions. As shown in Table I the susceptibility at 4.2 K decreases markedly with increasing Mn content; this is associated with the disappearance of ferromagnetism above 27 at. % Mn. Similar to the quenched alloys[1,3] the 22 at. % Mn target has a ferromagnetic Curie point of 290 K. The spin-glass state at 40 K is evidenced by a sharp decrease of the magnetization (obtained by integration of the ac susceptibility), by an inflection point in χ_{ac} which continues to increase above 40 K which differs from the previously reported[3] downturn in χ_{ac} occurring at 40 K. Furthermore, one also observed a time-dependent magnetization below 40 K and a displaced hysteresis loop (Fig. 1) when cooling in −250 Oe from above 40 to 4.2 K. The coercive fields of 180 and 340 Oe were, however, larger than those of quenched alloys[1] while the saturation magnetization at 4.2 K and 2.5 kOe of 11 emu g^{-1} is much smaller than in quenched alloys ($\simeq$45 emu g^{-1}). Since complete ferromagnetic alignment of Ni and Mn moments in such an alloy would correspond to 91 emu g^{-1}, this would imply that the spin-glass interaction dominates the ferromagnetic coupling to a greater degree in this inductively molten target than in the quenched alloys.

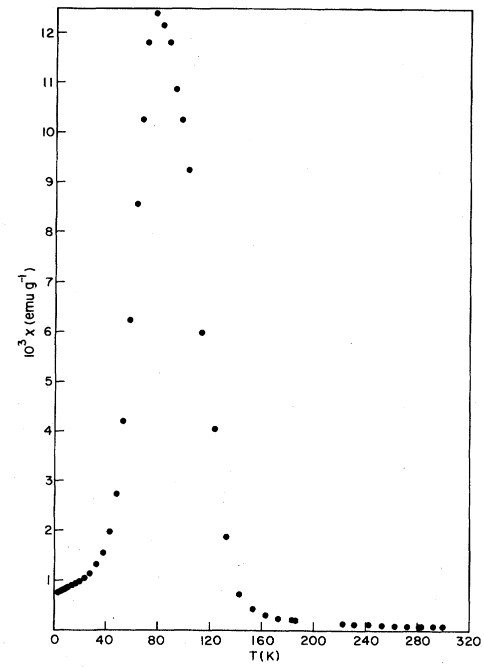

FIG. 2. χ_{ac} for the $Ni_{73}Mn_{27}$ target material as a function of T.

The 27 at. % Mn target displays a sharp susceptibility peak at 78 K as shown in Fig. 2. A plot of the high-temperature susceptibility follows a Curie-Weiss law [$\chi = C/(T-\Theta)$] with $\Theta = 125$ K and $n_{eff} = 1.5\mu_B$ which falls in between the Ni and Mn moments of, respectively, 0.3 and $3.2\mu_B$ measured[5] by neutron diffraction on Ni_3Mn. The value of 78 K for T_{SG} is very close to the value of 80 K measured on quenched alloys while the temperature range of infinite susceptibility (80–155 K) for quenched alloys overlaps the temperature interval between T_{SG} and Θ. This target displays also a displaced hysteresis loop upon field cooling.

The 31 at. % Mn target, similar to the quenched alloys, simply shows a typical spin-glass transition at 73 K. The T_{SG} of 73 K is, however, much lower than the 115 K reported for quenched alloys.[1] Since the differences between bulk alloys are, as shown later, trivial compared to those between films with different preparation conditions we will not discuss them any further.

TABLE I. Properties of Ni-Mn targets.

Target	a (Å)	$10^4\Delta a/c_{Mn}(\%)$[a]	$10^3\chi(4.2\text{ K})$ (emu g^{-1})	R[b]	T_{SG} (K)	Displaced loop
$Ni_{78}Mn_{22}$	3.577	6.8	14.7		40	Yes
$Ni_{73}Mn_{27}$	3.591	7.0	0.76	16.3	78	Yes
$Ni_{69}Mn_{31}$	3.601	7.1	0.12	2	73	

[a] $\Delta a = (a_{Ni\text{-}Mn} - a_{Ni})/a_{Ni}$; $a_{Ni} = 3.5238$ Å.
[b] $R = \chi(T_{SG})/\chi(4.2\text{ K})$.

TABLE II. Properties of $Ni_{78}Mn_{22}$ films.

Sample No.	T_D (K)	a (Å)	Rate (Å/min)	t[a] (μm)	$10^3\chi(4.2\ K)$ (emu g^{-1})	T_c[b] (K)	T_{SG} (K)	Displaced loop
1	77							
	ANN. RT[c]	3.567	50	2.1	5.4	270	60	Yes
2	77	Amorphous	8.5	0.3		200	58	No
	ANN. RT	3.583	8.5	0.3	2.6		58	
3	750	3.579	62	3	9.5	300	60	Yes
4	1173	3.590	350	16.8	0.2	240	78	No

[a]Film thickness.
[b]Ferromagnetic Curie point.
[c]Annealed at room temperature.

The properties of films with 22, 27, and 31 at. % Mn are listed, respectively, in Tables II, III, and IV. Only a few typical magnetic properties will be illustrated in the figures. It is clear from Tables II—IV that despite some irregularities, the lattice parameter a increases with increasing T_D which would imply from the correlation shown in Table I for bulk alloys that the amount of Mn in solution increases with T_D. Moreover, films deposited and kept at 77 K have the lowest lattice parameter even lower than that of the corresponding target. Unfortunately, as shown in Tables II—IV there is no obvious correlation between the magnetic properties and the lattice parameter. The magnetic properties are most sensitive to T_D, i.e., films deposited close to the order-disorder temperature (750 K for 22 at. % and 873 K for 27 and 31 at. %) show the greatest amount of ferromagnetism and a pronounced displaced hysteresis loop while films deposited at 77 K (whether amorphous or not) display the most ideal spin-glass behavior without displaced hysteresis loop. Since the magnetic properties depend strongly on composition, they will be discussed separately for each composition.

Films with 22 at. % Mn, similar to the target, exhibit both ferromagnetism and a spin-glass transition (Table II). The spin-glass transition is usually indicated by an inflection point in χ_{ac} and a sharp decrease of the magnetization. However, in the case of $Ni_{78}Mn_{22}$ No. 2 which was amorphous in the as-deposited state, the peak in the susceptibility at $T_{SG}=58$ K corresponds to the decrease in the magnetization (Fig. 3). Furthermore, this film did not display a displaced hysteresis loop while $Ni_{78}Mn_{22}$ No. 1 which is a thicker film deposited at 77 K at a higher rate (Table II) did. The most pronounced displaced hysteresis loop as well as the largest amount of ferromagnetism [as shown by the value of $\chi(4.2\ K)$ in Table II] is observed in $Ni_{78}Mn_{22}$ No. 3 which was deposited at 750 K, close to the order-disorder temperature. The displaced hysteresis loop for such a film is compared in Fig. 1 with that of the respective target. On the other hand, $Ni_{78}Mn_{22}$ No. 4 deposited well above the order-disorder temperature and quenched to 77 K displayed no displaced loop when cooled in 500 Oe and a very low χ_{ac} (4.2 K). Since the quenching rates through the order-disorder temperature are much greater in the present experiments than in the water-quenched alloys,[1–3] one can expect that films quenched from 1173 to 77 K are much more disordered than the water-quenched alloys. While the T_{SG} for films deposited at 77 and 750 K are all about the same ($\simeq$60 K) and well above that of the target (40 K), the film deposited at 1173 K displays the highest $T_{SG}\simeq78$ K possibly because it has the largest amount of randomly distributed Mn. While the same correlation exists for the 27 at. % Mn films (Table III) it is not true for the 31 at. % Mn films (Table IV). However, in all the compositions studied here, films quenched from 1173 K displayed the lowest χ_{ac}(4.2 K) and the value of χ_{ac}(4.2 K) decreases

TABLE III. Properties of $Ni_{73}Mn_{27}$ films.

Sample No.	T_D (K)	a (Å)	Rate (Å/min)	t (μm)	$10^3\chi(4.2\ K)$ (emu g^{-1})	R	T_{SG} (K)	Displaced loop
1	77	3.562	29	0.93	1.14	12.8	55	No
	ANN. RT	3.590	29	0.93	2.4	5.4	55	No
2	77							
	ANN. RT	3.586	10	0.37	5.8	5.8	88	
3	77							
	ANN. RT	3.586	32	0.22	4.7	7.7	85	
4	300	Amorphous	30	0.25	7.1	13.2	60	No
5	300	3.584	33	0.22	4.5	5.9	88	
6	573	3.589	292	4.5	2.9	7.7	63	Yes
7	873	3.596	323	4.6	9.2	1.7	88	Yes
8	1173	3.605	69	1.65	0.16			
9	1173	3.610	314	11.8	0.14	6.0	98	Yes

TABLE IV. Properties of $Ni_{69}Mn_{31}$ films.

Sample No.	T_D (K)	a (Å)	Rate (Å/min)	t (μm)	$10^3\chi(4.2\ \mathrm{K})$ (emu g^{-1})	R	T_{SG} (K)	Displaced loop
1	77	Amorphous	38	1.4	0.13	9.6	63	
2	77	Amorphous	63	2.1	0.10	2.2	58	
3	77	3.546	37	5.1	0.07	5.4	83	
	ANN. RT	3.603	37	5.1	0.18	6.4	83	
4	260	3.609	19	2.1	0.51	4.7	83	
5	300	3.621	15	0.6	1.26	8.3	56	
6	300	3.623	60	0.7	0.95	2.1	53	
7	573	3.617	265	6.85	0.21	2.3	48	
8	873	3.617	402	17.3	0.26	1.2	40	Yes
9	1173	3.630	125	3.0	0.09	2	36	
10	1173	3.619	423	19.7	0.05	1.6	33	

with increasing Mn content.

The magnetic properties of films with 27 at. % Mn are summarized in Table III and the dramatic effect of deposition conditions on their susceptibility is illustrated in Fig. 4 where one should notice that the ordinate scale only applies to closed- and open-circle data. It is clear from Fig. 4 that the effect of T_D is small on T_{SG} (55 to 98 K) but large on the value of χ_{ac} which varies by almost two orders of magnitude. In particular annealing at RT (open versus closed circles in Fig. 4) leaves T_{SG} unchanged but doubles $\chi(4.2\ \mathrm{K})$. It is also interesting to point out that although the amorphous film No. 4 has the highest value of $\chi(4.2\ \mathrm{K})$ next to No. 7 which was deposited close to the order-disorder temperature, No. 4 does not display a displaced hysteresis loop while No. 7 does (Table III). One may therefore conclude that a displaced hysteresis loop is not necessarily linked to a high value of $\chi(4.2\ \mathrm{K})$ but rather to a specific structure of the film when T_D is close to the order-disorder temperature. Indeed, No. 6 deposited at 573 K has a similar value of $\chi(4.2\ \mathrm{K})$ than No. 1 after anneal at RT (Table III) and the former displays a displaced hysteresis loop while the latter does not. The coercive fields pertaining to the displaced hysteresis loop observed on No. 6 are plotted in Fig. 5 as a function of increasing temperature: After cooling to 4.2 K in -15 kOe the hysteresis loop is asymmetric with respect to the origin ($H_c = 500$ and 700 Oe) and this asymmetry diminishes with increasing temperature and vanishes at 28 K. On the

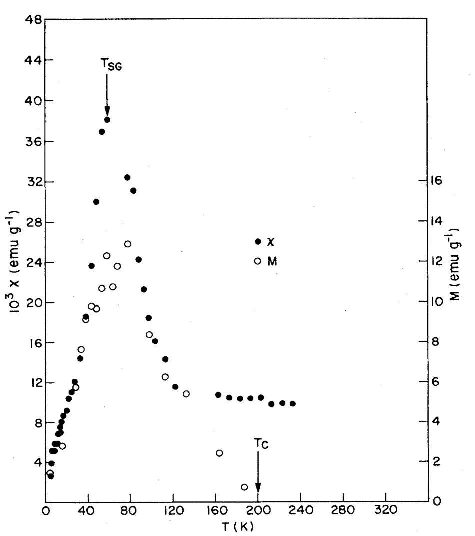

FIG. 3. χ_{ac} and magnetization (M) for $Ni_{78}Mn_{22}$ No. 2 as a function of T. M was measured in the amorphous state by cooling from $T_D = 77$ to 4.2 K and warming up while χ_{ac} was measured after anneal at RT.

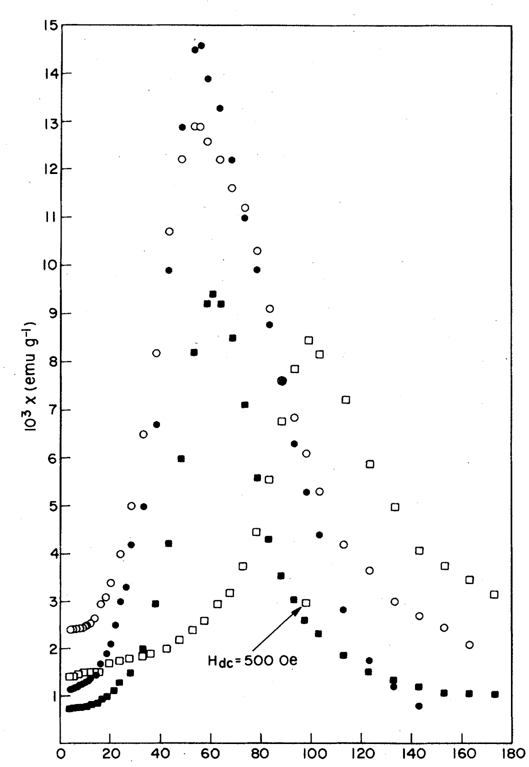

FIG. 4. χ_{ac} versus T for various $Ni_{73}Mn_{27}$ films: No. 1 as-deposited at 77 K (closed circles); No. 1 annealed 48 h at RT (open circles); No. 4 deposited at 300 K (solid squares, χ values have been multiplied by 0.1); No. 9 deposited at 1173 K (open squares, χ values have been multiplied by 10).

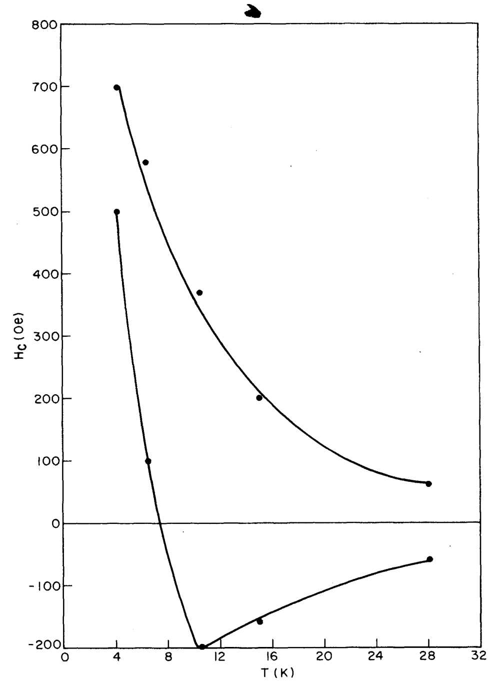

FIG. 5. Coercive fields (H_c) as a function of increasing temperature after cooling $Ni_{73}Mn_{27}$ No. 6 in a field of -15 kOe from 173 to 4.2 K. The curves are only a guide for the eyes.

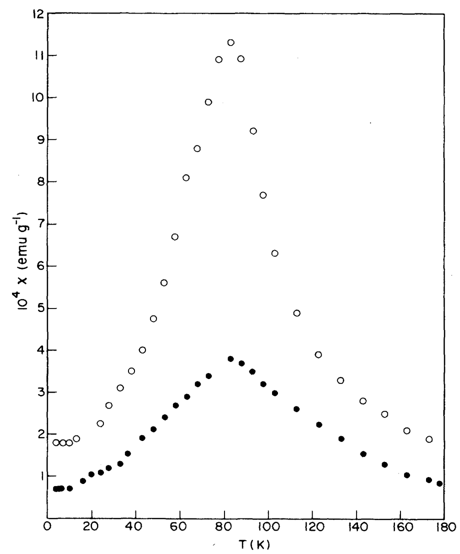

FIG. 6. χ_{ac} versus T for $Ni_{69}Mn_{31}$ No. 3 film: as-deposited at 77 K (solid circles); annealed 16 h at RT (open circles).

other hand, film No. 9 which was quenched from 1173 K is characterized by the lowest χ(4.2 K) but in contradistinction with $Ni_{78}Mn_{22}$ No. 4 ($T_D = 1173$ K) it does display a displaced loop. Furthermore, as in all typical spin-glasses, the χ peak is virtually eliminated by a small dc field (Fig. 4). The various values of T_{SG} corresponding to various T_D range from 55 to 98 K (Table III) which is close to both the T_{SG} of the respective target (Table I) and to that of the quenched alloy[1] (80 K).

Finally, turning our attention to films with 31 at.% Mn, the range of T_{SG} values (Table IV) overlaps with the T_{SG} of the corresponding target (73 K) but is distinctly lower than that reported for quenched alloys[1] (115 K). Since the composition of the target was accurately controlled as shown by the value of the lattice parameter (Table I) such differences must arise from preparation conditions. Indeed, the variation of T_{SG} with T_D seems to increase with increasing Mn content (34% for 22 at.% Mn, 78% for 27 at.% Mn, and a factor of 2.5 for 31 at.% Mn). Moreover, the change in χ upon annealing at RT a film deposited at 77 K is more pronounced in the 31 at.% Mn films than is the 27 at.% Mn films. This can be seen by comparing the data shown in Fig. 6 for a 31 at.% Mn film with that shown in Fig. 4 for a 27 at.% Mn film. Similar to $Ni_{73}Mn_{27}$ No. 1, annealing $Ni_{69}Mn_{31}$ No. 3 leads to a large increase in the lattice parameter and in χ while leaving T_{SG} unchanged.

IV. CONCLUSIONS

First of all, the presence of ferromagnetism in alloys with $c_{Mn} < 26$ at.% does not depend on preparation conditions. Although different preparation conditions result in widely different magnetic properties [different T_{SG}, different χ and $\chi(T)$, absence or presence of a displaced hysteresis loop] there is not a simple correlation between most magnetic properties and T_D. One can, however, establish a few correlations between certain magnetic properties and certain preparation conditions. The most ideal spin-glass behavior, i.e., a χ peak without a displaced hysteresis loop is always observed in films deposited at 77 K whether amorphous or not. Most interestingly this behavior is even found in films displaying a ferromagnetic transition ($Ni_{78}Mn_{22}$ No. 2). The greatest amount of ferromagnetism and the most pronounced displaced hysteresis loops are found in films deposited close to the order-disorder temperature. Films deposited at 1173 K and quenched to 77 K display the lowest susceptibility values. The presence of a displaced hysteresis loop is independent of the presence or absence of a ferromagnetic transition and of the magnitude of χ. The absence of a displaced hysteresis loop in films deposited at 77 K as well as similar observations previously reported on crystalline Cu-Mn films[6] suggest that a displaced hysteresis loop is the result of a specific structure and is not necessarily linked to the spin-glass state.

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