Effect of *d*-band mixing in Mn—transition-metal spin glasses

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The recently reported magnetic properties of amorphous (*a*) Mn-Zr alloys exhibited two remarkable and unexpected results. First, while Ni, Co, and Fe display no local magnetic moment when alloyed with Zr in metallic glasses, Mn has a local moment in *a*—Mn-Zr. Second, the existence of the Mn local moment does not result in a spin-glass interaction. These results can be understood by the study of the magnetic properties of *a*—Cu-Zr-Mn alloys presented here which shows that the absence of spin-glass interaction in *a*—Mn-Zr is not due to the amorphous state but to a mixing of the Zr and Mn *d* bands. This explanation suggests that a spin-glass interaction should exist when the transition-metal host for Mn displays a low density of *d* states at the Fermi level (E_F). Indeed, among transition metals, W has the lowest density of *d* states at E_F, and W-Mn alloys exhibit a spin-glass transition. The susceptibility of this new spin glass was measured in low ac field and in both low and high dc fields. The spin-freezing temperature (T_{SG}) increases essentially linearly with Mn content up to 34 at. % Mn where massive antiferromagnetism sets in.

I. INTRODUCTION

We recently reported[1] the magnetic properties of amorphous (*a*) Mn-Zr alloys which exhibited two remarkable and unexpected results. First, while Ni, Co, and Fe display no local magnetic moment[2] when alloyed with Zr in metallic glasses, Mn has a local moment in *a*—Mn-Zr. Second, despite the existence of a Mn local moment, no spin-glass interaction could be detected in amorphous alloys with 1—67 at. % Mn. What is meant here by the absence of spin-glass interaction is that while in Cu-Mn, Ag-Mn, etc. there exists a distribution of exchange wide enough and strong enough to lead to spin freezing into a random configuration, in *a*—Mn-Zr the distribution may be wide enough but the overall exchange is too weak to give ordering. In order to understand whether the absence of a spin-glass interaction is caused by amorphousness or by an interaction between the Mn and Zr *d* states, a study of the magnetic properties of *a*—Cu-Zr-Mn alloys will be presented here. Indeed, Cu-Mn is an archetypical spin glass[3] and the disappearance of the spin-glass interaction in the ternary alloys with increasing Zr content should shed some light on the absence of such interaction in *a*—Mn-Zr. It is, by the way, doubtful that the absence of spin-glass interaction in *a*—Mn-Zr alloys is due to amorphousness, since amorphous Au-Si-Mn alloys displayed spin-glass transitions very similar to those of crystalline Au-Mn.[4]

The present study is divided in two parts. The first part deals with the ternary *a*—Cu-Zr-Mn alloys and shows the dependence of the spin-freezing temperature (T_{SG}) and of the manganese spin state as a function of Zr content at fixed Mn content. The second part consists of an extensive study of the magnetic properties of a new spin-glass alloy: W-Mn.

II. EXPERIMENTAL PROCEDURE

All the Cu-Zr-Mn and Ti-Mn films were sputtered from arc-melted master alloy cathodes onto sapphire substrates mostly at 260 K and in a few cases at 77 K. The W-Mn films were sputtered from three different types of cathodes: a grooved tungsten rod with manganese molten in the grooves, a manganese disk with a variable number of tungsten wires wrapped around, and pressed powders. In the latter case both 325 and 100-mesh powders were used, tumbled and pressed in the form of a disk. The resulting disk which crumbles easily was consolidated by sintering for 1.5 h at 1100 °C in a hydrogen atmosphere. The W-Mn films were deposited at 260 and 77 K. The sputtering powder was 15 W (1500 V, 10 mA) for films deposited at 260 K and 2.25 W (1500 V, 1.5 mA) for films deposited at 77 K. Mo-Mn films and Cr-Mn films were sputtered from pressed powder cathodes prepared in a similar manner to the W-Mn cathodes. The structure of the films was established by x-ray diffraction and their composition was determined by x-ray fluorescence analysis calibrated by atomic absorption analysis.

The deposited films were then scraped with a sapphire slide in order to avoid magnetic contamination. The susceptibility of the resulting flakes was measured in a high dc magnetic field using the Faraday method, in a low dc field (3 Oe) in a susceptometer using a superconducting quantum-interference device (SQUID), and in a low ac field (4 Oe) at 10 kHz.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Study of ternary $(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$ alloys

The major results of this study are shown in Fig. 1, which displays the well-known susceptibility cusps

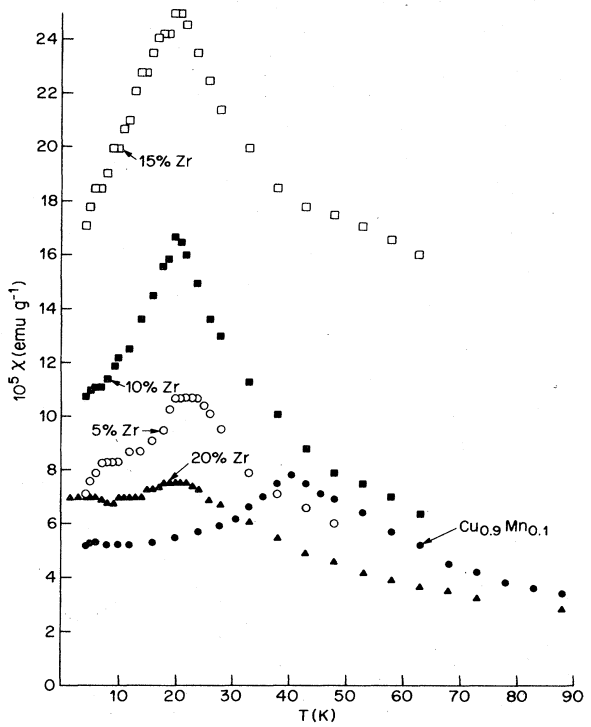

FIG. 1. Temperature dependence of the ac susceptibility as a function of the amount of substituted Zr in $(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$.

characteristic of a spin-glass interaction for a crystalline film of the archetypical Cu-Mn spin-glass[3] and for *amorphous* Cu-Mn-Zr films. Since, as shown in Fig. 1, the ternary amorphous $(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$ alloys display a spin-glass transition for $x \leq 0.2$, it is clear that the absence of spin-glass interaction in a—Mn-Zr cannot be linked to the amorphous state. This point will be further discussed in the discussion of the magnetic properties of crystalline Ti-Mn alloys. Furthermore, it is also clear from Fig. 1 that the spin-glass cusp has almost vanished when 20 at. % Zr is substituted for Cu. This is further discussed in Fig. 2, where one notices that with increasing

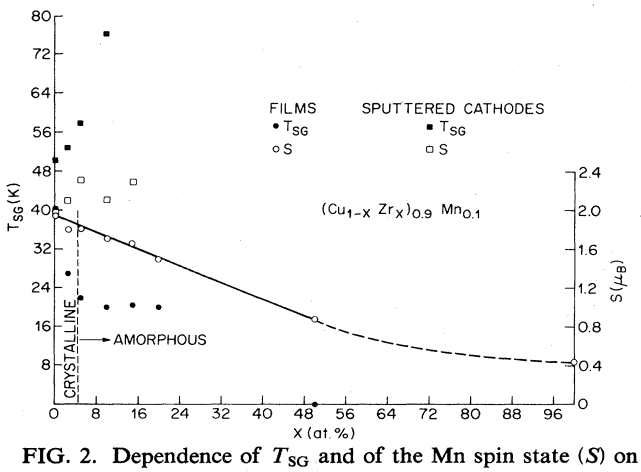

FIG. 2. Dependence of T_{SG} and of the Mn spin state (S) on substituted Zr for both films and sputtering cathodes.

Zr the spin-state (S) decreases smoothly from that of $Cu_{0.9}Mn_{0.1}$ to that reported[1] for $Zr_{0.9}Mn_{0.1}$. On the other hand, the spin-freezing temperature (T_{SG}), which corresponds to the maxima in the susceptibility curves of Fig. 1, remains constant for amorphous films up to the disappearance of the spin-glass transition which occurs for Zr concentrations larger than 20 at. %. The constancy of T_{SG} reflects the fixed Mn concentration, and the decrease in S can be understood in terms of the decrease in the Mn moment by the mixing of the unfilled Mn and Zr d bands. This latter point can be further reinforced by the summary of magnetic parameters obtained by the Faraday method listed in Table I.

The data described in Table I pertain to two different types of ternary alloys: for substituted Zr concentrations of 5 at. % and more the films are amorphous; when less than 5 at. % the films are crystalline even when deposited at 77 K. However, as shown in Table I, the magnetic properties vary smoothly with increasing Zr concentrations irrespective of the structural state of the films. Only the binary $Cu_{0.9}Mn_{0.1}$ alloy displays a high positive Curie-Weiss temperature (Θ) as previously reported[5,6] and a low Van Vleck—temperature—independent contribution χ_0. Even a small 2.5 at. % Zr substitution increases χ_0 to a large value similar to that reported for a—Mn-Zr alloys.[1] The low value of χ_0 for Cu alloys is due to the filled Cu d band, and the increase in χ_0 with Zr substitution is due to the presence of an unfilled Zr d band. Indeed, a progressive increase of χ_0 with increasing Zr towards the value of pure Zr has been previously reported in Cu-Zr alloys.[2] But the most striking effect shown in Table I is the progressive decrease in p_{eff} (p_{eff} and Θ are determined from the high-temperature slope of a Curie-Weiss fit over the temperature range ΔT specified in Table I) with increasing Zr concentration, and below a value of p_{eff} of approximately $3.9\mu_B$ ($S \simeq 1.5\mu_B$) the spin-glass interaction disappears. It is clear from Table I that this effect is independent of the structure of the film since an amorphous film with 5 at. % Zr substituted has the same p_{eff} value as a crystalline film with 2.5 at. % Zr. At a concentration of 50 at. % of substituted Zr, the magnetic properties of the ternary alloys become similar in all respects to the binary a—Mn-Zr alloys:[1] i.e., as the Curie-Weiss fit is extended to lower temperatures both p_{eff} and Θ decrease while the temperature-independent contribution χ_0 increases. This reflects the antiferromagnetic pairing of many Mn spins at low temperatures. One should note from Table I that such a behavior is not observed in the ternary alloys with $x \leq 20$ at. % which display a spin-glass transition (Figs. 1 and 2). A comparison of the magnetic properties of the two amorphous ternary alloys with $x = 20$ at. % Zr and $x = 50$ at. % Zr (Table I) clearly establishes that the disappearance of the spin-glass transition in a—$(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$ and the absence of a spin-glass transition in a—Mn-Zr is not caused by the amorphous structure but by a decrease in the Mn spin-state as a result of the mixing of Zr and Mn d bands.

Another interesting point revealed by the data shown in Fig. 2 is the opposite behavior of films and the master alloy cathodes used in their deposition: In the latter case T_{SG} increases while S remains essentially constant with

TABLE I. Magnetic properties of $(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$ alloys.

Zr content x (at. %)	T_D[a] (K)	p_{eff} (μ_B)	$-\Theta$ (K)	χ_0 (10^{-6} emu/mol)	$\chi_{300\,K}$ (10^{-6} emu/mol)	ΔT[b] (K)
0[c]	260	4.33	−30	89	987	150—350
		4.45	−24	58		100—350
		4.67	−16	−0.7		75—350
2.5[c]	260	4.39	3	704	1470	60—300
		4.42	4	695		50—300
		4.49	6	670		40—300
2.5[c]	77	4.18	0	308	1056	60—300
		4.24	2	291		50—300
		4.29	4	279		40—300
5	260	4.51	−7	236	1140	50—300
		4.50	−7	242		40—300
10	260	4.31	1	195	963	80—380
		4.32	1	194		40—380
		4.39	3	170		25—380
15	260	4.20	3	369	1110	50—300
		4.20	4	360		40—300
		4.26	5	349		30—300
20	260	3.87	10	240	845	80—310
		3.87	10	240		40—310
		3.84	9	247		25—310
		3.97	13	208		15—310
50	260	2.59	18	248	507	40—300
		2.47	12	271		25—300
		2.32	6	304		10—300

[a]Temperature of deposition.
[b]Temperature of Curie-Weiss fit.
[c]Crystalline films; all other films are amorphous.

increasing Zr concentration. This results from the fact that Zr is insoluble in both Mn and Cu and, consequently, in these phase-separated cathodes, increasing Zr implies an increasing Mn-to-Cu ratio, which leads[3] to an increase in T_{SG}. This result stresses the necessity of obtaining single-phase alloys by film deposition. This point is further demonstrated in Fig. 2 by the values of S and T_{SG} for the 2.5 at. % Zr crystalline film which fall in between those for crystalline $Cu_{0.9}Mn_{0.1}$ and those for the amorphous alloys films.

The absence of a spin-glass state has also been observed in Ti-Mn films. Contrary to the Mn-Zr films,[1] these films are crystalline. X-ray diffraction reveals that the Ti-Mn films are a solid solution of Mn in Ti with an [011] preferred orientation. Consequently, the absence of spin-glass interaction which is now observed in single-phase crystalline alloys is again attributed to a mixing of Mn d states with partially filled Ti d band. This point is supported by the high-field magnetic properties of crystalline Ti-Mn alloys shown in Table II, which can be seen to be very similar to those a—Mn-Zr alloys.[1] Indeed, as the Curie-Weiss fit is restricted to lower temperatures, both Θ and p_{eff} decrease while χ_0 increases. Furthermore, similar to a—Mn-Zr alloys, increasing the Mn content increases

TABLE II. Magnetic properties of various Mn alloys.

	T_D[a] (K)	p_{eff} (μ_B)	$-\Theta$ (K)	χ_0 (10^{-6} emu/mol)	$\chi_{300\,K}$ (10^{-6} emu/mol)	ΔT[b] (K)
$Ti_{82}Mn_{18}$	77	2.45	30	218	623	40—300
		1.80	6	590		10—100
$Ti_{50}Mn_{50}$	77	1.04	17	2510	2860	20—300
$Cr_{80}Mn_{20}$	260	1.19	45	652	1150	50—300
Cr	260	1.09	43	382	810	50—300
$Mo_{92}Mn_8$	260	3.89	7	561	1067	10—300
$W_{91}Mn_9$	260	5.23	1	6.4	1062	20—300

[a]Temperature of deposition.
[b]Temperature of Curie-Weiss fit.

the antiferromagnetic pairing, as shown by the decrease in p_{eff} and the increase in χ_0.

In conclusion, the absence of a spin-glass interaction in certain Mn—transition-metal (TM) alloys (TM=Ti,Zr) is caused by a mixing of the Mn d states with the partially filled TM d bands. Such mixing effect cannot obviously take place in the canonical spin glasses Cu-Mn, Ag-Mn, and Au-Mn because the host TM's (Cu, Ag, and Au) have a full d band. However, one may still observe a spin-glass interaction even when the host TM has a partially filled d band, as long as the density of d states at the Fermi level is small. A measure of this density of d states is the specific-heat parameter γ, which is 3.36 and 2.77 mJ/g-at. K^2 for Ti and Zr, respectively, but is minimal for elements in column VIB: 1.42, 1.83, and 1.01 mJ/g-at. K^2 for Cr, Mo, and W, respectively.[7] In particular, this suggests W as the most likely candidate for a spin-glass alloy with Mn because the density of d states is a minimum at the Fermi level, and may, therefore, not perturb the Mn d band. This possibility will be examined in the next section.

B. A new spin-glass alloy: W-Mn

The W-Mn films, whether deposited at 260 or 77 K, are a crystalline solid solution of Mn in W with a [110] preferred orientation. Using the single diffraction peak of the films as an interpolation between the W(110) peak and the Mn(330) peaks yields a Mn concentration within 10% of the concentration obtained by atomic absorption analysis.

The possibility that the low density of W d states may not perturb the Mn d band is supported by the data shown in Table II. Indeed, the high p_{eff} and the low χ_0 value measured on $W_{91}Mn_9$ are very similar to the corresponding values for Cu-Mn alloys (Ref. 3 and Table I). As a result, W-Mn alloys exhibit a spin-glass transition (Figs. 3 and 4). Figure 3 displays the typical ac susceptibility peak and the rounding off of the peak by the application of a dc magnetic field. One may notice that even with $H_{\text{dc}}=0$ the peak is still somewhat rounded. This smearing of the peak is undoubtedly due to the fact that the films are sputtered from fairly inhomogeneous cathodes, which results in a composition spread of about $\pm 10\%$ from the average composition quoted for a given film. Since, as shown in Fig. 5, $dT_{\text{SG}}/dC_{\text{Mn}} \simeq 1$, such a concentration spread could easily account for the 2—3 K width of the peak shown in Fig. 3. The typical irreversibility displayed by spin glasses is depicted in Fig. 4: When cooled in zero field, the low-field ($H=3$ Oe) dc susceptibility is identical within experimental error to the ac susceptibility; when cooled in a field, the dc susceptibility becomes irreversible, although the spin-glass peak is still observable. The irreversible data shown in Fig. 4 ($H_{\text{cool}}=3$ Oe) represent the instantaneous measurement of the susceptibility after cooling in 3 Oe to a given temperature. Removing the cooling field results in a slow decay of the irreversible magnetization with time. The decay was observed over a period of 10 min. One notices also in Fig. 4 that the field-cooled curve and the zero-field-cooled curve diverge above T_{SG}. This could arise either from the compositional inhomogeneity of the films discussed above or from an upward curvature at low field of the M-versus-H curve. The spin-glass properties of the W-Mn

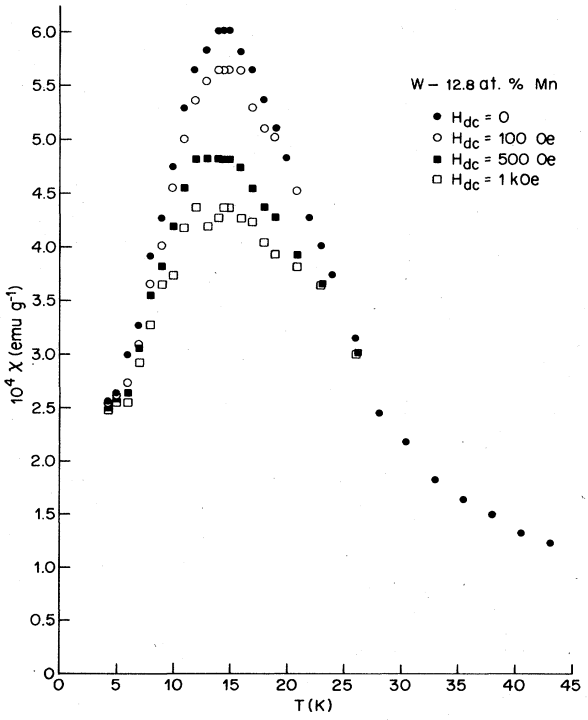

FIG. 3. Temperature dependence of the ac susceptibility as a function of applied dc magnetic field.

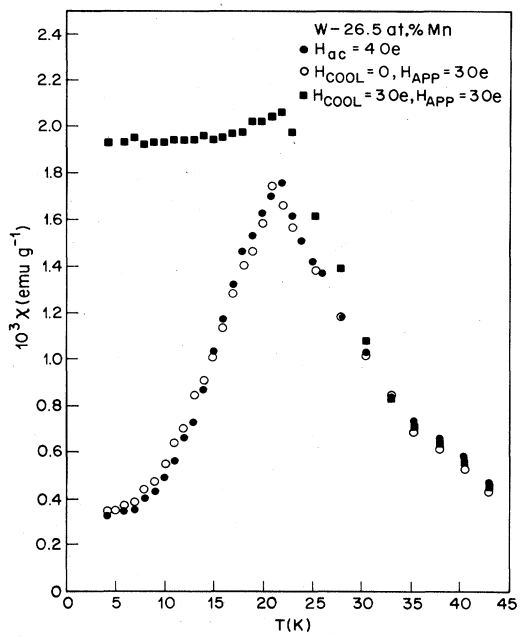

FIG. 4. Temperature dependence of the ac and dc susceptibilities; the dc susceptibility was measured in both zero-field-cooled and field-cooled modes. One should also note that the dc susceptibility was obtained from M/H and not from the slope of the M,H curve.

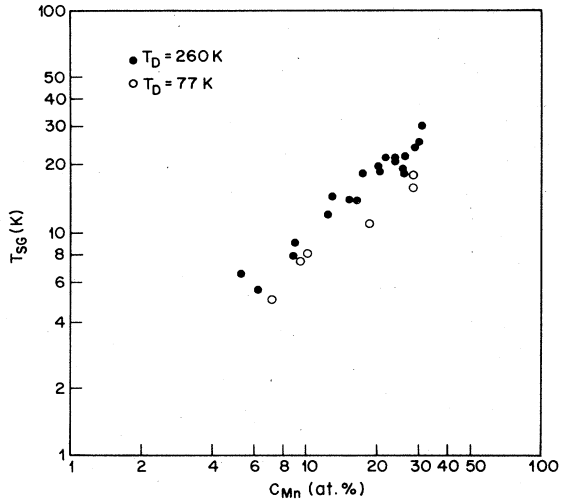

FIG. 5. Dependence of the spin-glass freezing temperature (T_{SG}) on Mn concentration for films deposited at $T_D = 260$ and 77 K.

system are summarized in Fig. 5. The value of T_{SG} depends only weakly on T_D: Films deposited at 77 K have a lower T_{SG} than films deposited at 260 K, but the concentration dependence of T_{SG} remains essentially the same. The antiferromagnetic pairing increases with increasing Mn content as shown by the decrease in p_{eff} up to 34 at. % Mn, where the spin-glass state disappears to be replaced by massive antiferromagnetism.

Since Cr and Mo also display a low density of d states at the Fermi level (although appreciably higher than W), one should also seek a spin-glass interaction in Cr-Mn and Mo-Mn alloys. However, no such interaction was found in either alloy. In the case of Cr, which next to W has the lowest density of d states, it is not surprising since the host is itself antiferromagnetic. Indeed, as shown in Table II, the magnetic properties of $Cr_{80}Mn_{20}$ are very similar to those of pure Cr and are strongly antiferromagnetic: low p_{eff} and high negative Θ and high χ_0 values. This is in agreement with the antiferromagnetic behavior previously reported in bulk Cr-Mn alloys.[8,9] In the case of Mo, which has the highest density of d states in column VIB (approximately twice that of W), the magnetic properties of $Mo_{92}Mn_8$ (Table II) are intermediate between those of W-Mn and those of Mn-Zr. Like Mn-Zr, Mo-Mn has a high χ_0 value and, interestingly, the value of p_{eff} for $Mo_{92}Mn_8$ is precisely the value where the spin-glass interaction vanishes in $(Cu_{1-x}Zr_x)_{0.9}Mn_{0.1}$ alloys (see $x = 20$ in Table I). Consequently, only W has a low enough density of d states to leave the Mn d states unperturbed.

IV. CONCLUSIONS

The absence of a spin-glass interaction in Mn-Zr and Mn-Ti alloys as well as the disappearance of this interaction in Cu-Mn-Zr alloys with increasing Zr concentration has been linked to a mixing of the Mn and Zr or Ti partially filled d bands. This model has led to the discovery of a new spin-glass system: W-Mn. The spin-glass interaction can exist in this system because, although W also has a partially filled d band, the density of d states at the Fermi level is minimal.

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