Local Mn moment in amorphous Mn-Zr alloys

J. J. Hauser and J. V. Waszczak
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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While Ni, Co, and Fe display no local magnetic moment when alloyed with Zr in metallic glasses, Mn has a local moment in Mn-Zr, Mn-Zr-Cu, and Mn-Zr-Ni alloys. The moment decreases as Mn increases from 1 to 67 at.% as a result of increasing antiferromagnetic order and no spin-glass interaction could be detected. The Mn moment results in the disappearance of superconductivity at $\simeq 2$ at.% Mn while Ni-Zr and Fe-Zr glasses remain superconducting up to 60 at.% Ni and 28 at.% Fe. The superconducting properties of the host amorphous Zr-Ni and Zr-Cu films were similar to those of glasses obtained by melt spinning.

It is well known that crystalline Cu-Mn and Au-Mn solid solutions display a spin-glass interaction.[1,2] The spin-glass interaction has also been seen in amorphous Au-Si-Mn films.[3] On the other hand, metallic *M*-Zr glasses (M = Cu, Ni, Co, and Fe) have been prepared[4] by melt spinning. This suggested the investigation of a possible spin-glass interaction in amorphous Mn-Zr alloys. While *M*-Zr glasses (M = Ni, Co, and Fe) displayed no local magnetic moment,[4] we will show by both magnetic susceptibility and superconductivity measurements that Mn has a local moment in Mn-Zr, Mn-Zr-Cu, and Mn-Zr-Ni alloys. These local Mn moments do not, however, interact in a spin-glass state.

All the films were deposited by dc getter sputtering from arc-melted buttons of the desired composition. The deposition temperatures varied from 77 to 508 K depending on the alloy and the desired state of thermal relaxation of the material. The amorphous state was checked by x-ray diffraction and the composition by x-ray fluorescence analysis. For the magnetic susceptibility measurements, the material was deposited on sapphire substrates at 30 W (2000 V, 15 mA) and the material (usually from 50 to 120 mg) was scraped with a sapphire slide in order to avoid magnetic contamination. The resulting flakes were placed in an ultrapure quartz container and measured using the Faraday method.[5] The low field dc susceptibility was measured in a susceptometer using a superconducting quantum interference device. For the conductivity measurements, the alloy films with thicknesses varying between 2 and 5 μm (corresponding to 0.6–1.6 mg of material) were deposited at powers ranging from 15 to 30 W on sapphire substrates. The temperature of deposition (T_D) was chosen between 413 and 508 K for the Ni-Zr host alloys and 260 K for the Cu-Zr host alloys because these T_D's resulted in the maximum superconducting transition temperature (T_c).

Mn-Zr films can be deposited in the amorphous state at $T_D = 413$ K for Mn concentrations ranging from 15 to 67 at.%. The crystallization temperature (T_x) for a 32.5 at.% Mn film as determined by differential scanning calorimetry (DSC) was 703 K which is quite similar to the T_x of other *M*-Zr glasses[6,7] (M = Cu, Ni, Co, and Rh). $Mn_{10}Zr_{90}$ films can only be obtained in the amorphous state if deposited and kept at 77 K: they crystallize upon heating to room temperature. However, while *M*-Zr glasses (M = Cu, Ni, Co, and Fe) display superconducting properties[4] up to 60 at.% Cu, 67 at.% Ni, 47 at.% Co, and 28 at.% Fe the Mn-Zr films were not superconducting above 1 K irrespective of T_D. This last point is important since T_c depends markedly on T_D. For example, the T_c's for amorphous $Ni_{20}Zr_{80}$ films are < 1 K, 2.6, 3.2, and 3.4 K for the respective T_D's of 77, 260, 413, and 508 K. Associated with the increase in T_c is a marked decrease in resistivity down to 153 $\mu\Omega$ cm for $T_D = 508$ K. Both the T_c and ρ for the film deposited at 508 K are close to those reported for the glass.[4] Consequently, the absence of superconductivity in Mn-Zr films is not the result of some structural difference between films and glasses but must be caused by Mn. This will now be demonstrated by the susceptibility measurements discussed below.

The susceptibility of $Ni_{20}Zr_{80}$ shown in Fig. 1 is essentially temperature independent except for a small increase for $T < 50$ K in agreement with previous results[4,7,8] obtained on glasses prepared by melt spinning. This indicates that Ni does not have a local magnetic moment and the same conclusion was previously reached[4] for Co and Fe. On the other hand, it is quite clear from Fig. 1 that $Mn_{15}Zr_{85}$ displays a strongly temperature-dependent susceptibility which is well fitted by a Curie-Weiss law over the whole temperature range, thus establishing the existence of a Mn local moment. The deviations from the Curie-Weiss fit at low tem-

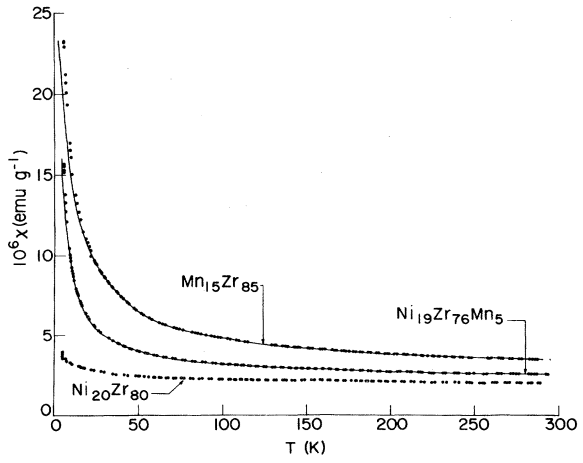

FIG. 1. Susceptibility as a function of temperature (dots) for $Ni_{20}Zr_{80}$ ($H = 4.3$ kOe), $Ni_{19}Zr_{76}Mn_5$ ($H = 4.3$ kOe), and $Mn_{15}Zr_{85}$ deposited at 77 K ($H = 12.8$ kOe). The solid lines are least-squares Curie-Weiss fits of the data with parameters shown in Table I.

TABLE I. Magnetic properties of amorphous Zr alloys.

Sample	T_D[a] (K)	p_{eff} (μ_B)	$-\theta$ (K)	χ_0 (10^{-6} emu/mole)	$\chi_{300\,K}$ (10^{-6} emu/mole)	ΔT[b] (K)
$Mn_{15}Zr_{85}$	77	1.00	8.5	241	302	10–300
		0.82	3.2	361		0–30
		0.77	2.6	408		0–15
$Mn_{15}Zr_{85}$	413	0.87	8.0	283	323	10–300
$Mn_{32.5}Zr_{67.5}$	413	0.83	12.0	358	442	10–300
		0.69	5.0	450		10–50
		0.74	7.0	401		0–50
		0.79	8.0	329		0–30
$Mn_{50}Zr_{50}$	413	0.87	14.0	979	1270	30–300
$Mn_{67}Zr_{33}$	413	0.72	13.5	1670	2030	0–250
$Ni_{20}Zr_{80}$	413	0	0	172	172	. . .
$Ni_{19.75}Zr_{79}Mn_{1.25}$	413	1.59	1.4	198	177	0–85
		1.33	0	263		0–15
$Ni_{19}Zr_{76}Mn_5$	413	1.06	2.2	196	213	0–300
		1.01	1.5	209		0–100
		0.96	1.0	231		0–30
$Cu_{19}Zr_{76}Mn_5$	260	1.48	1.5	174	189	0–100
		1.40	1.0	220		0–30

[a]Temperature of deposition.

[b]Temperature of range of Curie-Weiss fit.

peratures are caused by the antiferromagnetic pairing of many Mn spins. This is shown in Table I by the fact that as the Curie-Weiss fit is restricted to lower temperatures the Curie-Weiss temperature θ and $p_{eff}=2[S(S+1)]^{1/2}$ decrease while the temperature independent contribution χ_0 increases. It is also clear from Table I, that increasing the Mn content increases the antiferromagnetic pairing as shown by a decrease in p_{eff} and an increase in χ_0. It is also interesting to point out that $Mn_{15}Zr_{85}$ deposited at 77 K displays a larger value of p_{eff} and a smaller value of χ_0 than when deposited at 413 K (Table I) most probably because a lower T_D favors more free Mn spins as a result of the greater randomness. However, besides these antiferromagnetic interactions, there was no indication of any spin-glass interaction for Mn concentrations between 10 and 67 at.%. This is demonstrated by the low-field data shown in Fig. 2 for a 15 at.% Mn concentration: the susceptibility measured with 18 Oe is identical whether the sample is cooled in zero field or is cooled in the measuring field. Furthermore, except for a small increase in susceptibility with decreasing field, the Mn moment is essentially the same when measured in 12.8 kOe and in 18 Oe. Although the small field dependence of the χ is not a central issue in the present study, we will discuss it at greater length since it was the subject of a recent controversy in $Fe_{24}Zr_{76}$ glasses.[8,9]

Hedman and Rapp[8] argued that a weak-field dependence of the susceptibility which increases with decreasing temperature could be responsible for an apparent stronger temperature dependence of χ observed by Kaul.[9] Although the latter rejected this interpretation and although the small curvature shown by $\chi(T)$ in Fig. 1 for $Ni_{20}Zr_{80}$ is negligible compared to the strong Curie-Weiss dependence of alloys with Mn, the point is worth pursuing from the point of view of the origin of the field dependence. Indeed, both authors[8,9] were noncommittal on whether ferromagnetic inclusions and/or superparamagnetic clusters are responsible for the field dependence. The data shown in Fig. 3 for a variety of amorphous alloys suggest that the χ field dependence is an extrinsic effect (i.e., caused by ferromagnetic in-

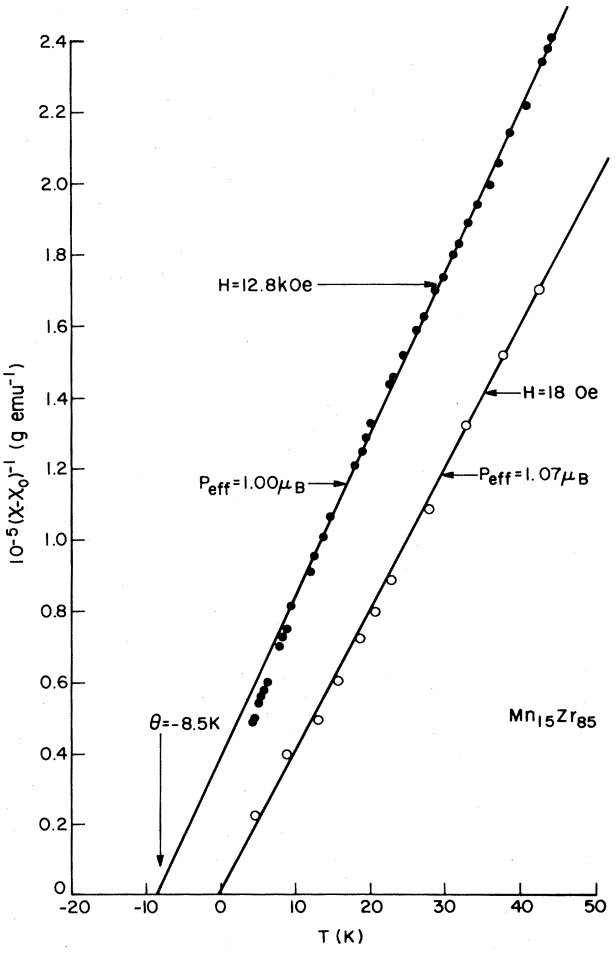

FIG. 2. Inverse susceptibility as a function of temperature for $Mn_{15}Zr_{85}$ deposited at 77 K with $\chi_0=2.808\times10^{-6}$ emu/g measured in high and low dc magnetic fields. The 12.8-kOe data are the same as shown in Fig. 1.

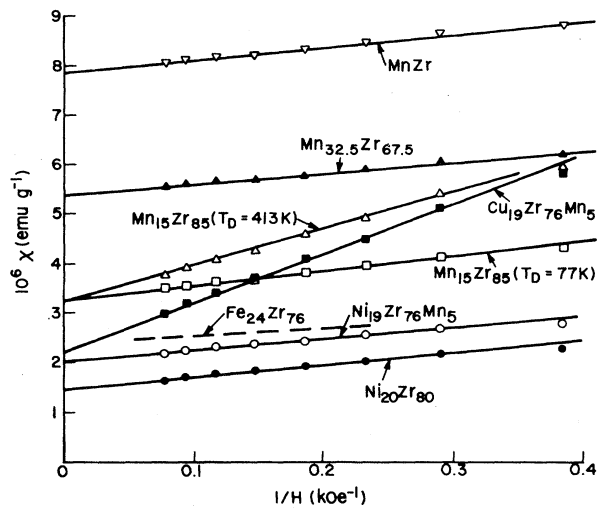

FIG. 3. Field dependence of the susceptibility at 300 K for various amorphous films. The dashed line approximates the data shown for the $Fe_{24}Zr_{76}$ glass in Ref. 8.

clusions). This statement is first supported by the fact that the dependence of χ on $1/H$ shown in Fig. 3 starting with $Ni_{20}Zr_{80}$, $Ni_{19}Zr_{76}Mn_5$, and with increasing amount of Mn in Mn-Zr alloys is essentially the same and similar to that reported[8] for $Fe_{24}Zr_{76}$. One would expect the clustering (intrinsic effect) if present to increase with increased Mn content. Furthermore, although $Mn_{15}Zr_{85}$ deposited at 413 K shows a stronger field dependence than $Mn_{15}Zr_{85}$ deposited at 77 K which would be consistent with the idea of increasing clustering with increasing T_D, the reverse is true for $Cu_{19}Zr_{76}Mn_5$ ($T_D = 260$ K) and $Ni_{19}Zr_{76}Mn_5$ ($T_D = 413$ K). One should also notice that in the cases of different field dependences, the value of χ at $1/H = 0$ is the same.

Having established that it is the Mn local moment which is responsible for the absence of superconductivity in amorphous Mn-Zr alloys with Mn $\geq$ 10 at.%, it would be desirable to extend the study to lower Mn contents. As mentioned above, this is not possible since Mn-Zr films with Mn $<$ 10 at.% are not amorphous. Consequently, the study will be extended by incorporating Mn in $Ni_{20}Zr_{80}$ and in $Cu_{20}Zr_{80}$ which are amorphous, superconducting, and do not exhibit a local moment.[4] The susceptibility for $Ni_{20}Zr_{80}$ with 5 at.% Mn shown in Fig. 1 is obviously well fitted by a Curie-Weiss temperature dependence with parameters listed in Table I. It is clear from Table I that the magnetic properties of $Ni_{20}Zr_{80}$ alloys with Mn are similar to Mn-Zr alloys. Namely, the degree of antiferromagnetic ordering as shown by the decrease in p_{eff}, increases with increasing Mn content. Furthermore, all the magnetic properties (p_{eff}, θ, and χ_0) of Ni-Zr-Mn alloys seem to be a reasonable extension of the magnetic properties of Mn-Zr alloys to lower Mn content (Table I). Moreover, the magnetic properties of $Ni_{19}Zr_{76}Mn_5$ are very similar to those of $Cu_{19}Zr_{76}Mn_5$ (Table I) except that the latter displays a somewhat larger moment. Since the degree of antiferromagnetic ordering increases with increasing Mn content, the maximum Mn effective moment ($1.59\mu_B$) is measured in the most dilute alloy and corresponds to a spin state of 0.44. This is appreciably lower than the value reported[10] for Mn in dilute crystalline Cu-Mn alloys (2.25) but is close to the value observed[3] in amorphous Au-Si-Mn. The low Mn moment may therefore be linked to crystalline disorder.

The study will now be completed by examining the superconducting properties of Ni-Zr-Mn and Cu-Zr-Mn amorphous alloys. The data are shown in Fig. 4 and in the case of Ni-Zr-Mn the T_c's were measured both resistively (ρ) and by susceptibility (χ). The susceptibility measurements yield a higher value of T_c and a broader transition than the resistive measurements mainly because the χ measurement is made on about two orders of magnitude more material than the resistive measurement. At any rate, the rate of depression of T_c with Mn is about the same for χ and ρ measurements. The data shown in Fig. 4 establish two important results: first, the T_c's of amorphous $Ni_{20}Zr_{20}$ and $Cu_{20}Zr_{20}$ films ($\simeq 3.6$ K) are in excellent agreement with those reported[4] for glasses and second, the strong depression of T_c with Mn (as high as 1.5 K/at.% Mn) clearly explains the absence of superconductivity in Zr glasses containing more than 5 at.% Mn. Furthermore, the superconducting data shown in Fig. 4 are consistent with the magnetic data of Table I. Namely, the depression of T_c with Mn is stronger in $Cu_{20}Zr_{80}$ than in $Ni_{20}Zr_{80}$ which is consistent with the lower Mn moment in the latter. Moreover, the rate of depression of T_c decreases with increasing Mn content as a result of increasing antiferromagnetic ordering (i.e., the number of Mn free spins does not increase linearly with the Mn content).

In conclusion, both superconducting and magnetic measurements have established the presence of a Mn local moment in Zr glasses. However, no spin-glass interaction could be detected.

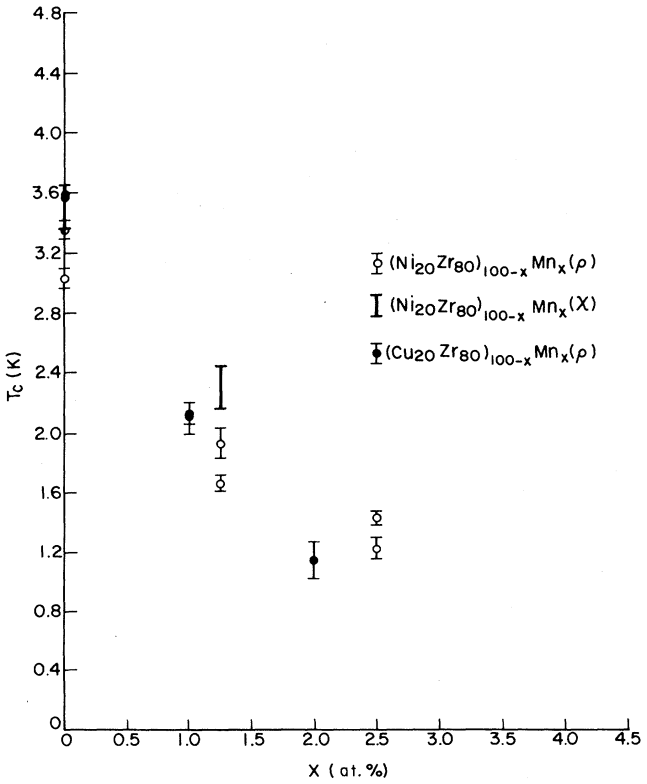

FIG. 4. Superconducting transition temperatures measured resistively (ρ) and by susceptibility (χ) as a function of Mn content.

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