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Magnetic susceptibility of an amorphous spin glass: Au-Si-Mn

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Amorphous films of $Au_{0.81-x}Mn_xSi_{0.19}$ with $x = 0.02$, 0.05, and 0.10 were deposited at 77 K by getter-sputtering. The low-temperature ($T < 77$ K) magnetic susceptibility (χ) was measured on the as-deposited films and as a function of annealing. The susceptibility of the as-deposited film is about an order of magnitude lower than that reported for bulk $Au_{0.95}Mn_{0.05}$, and the susceptibility peak is also much smaller [the ratio $R = \chi_{max}/\chi(4.2\text{ K})$ is about 1.5 as compared to 4 for bulk]. Annealing the films at 293 K (which leaves the films amorphous) increases χ by a factor of 5 and R to about 2. The most striking effect is observed after annealing at 373 K; the films are still mostly amorphous as determined by electrical resistivity, x-ray diffraction, and differential thermal analysis, but R increases to values between 4 and 9. The reasons for this effect cannot be ascribed entirely to the presence of Si nor to partial recrystallization, since similar annealing effects were observed in crystalline $Au_{0.95}Mn_{0.05}$ films.

I. INTRODUCTION

Typical crystalline spin-glass alloys are the solid solutions Cu-Mn, Au-Mn, and Au-Fe which are characterized by a sharp cusplike peak in the magnetic susceptibility[1-3] occurring at low temperatures. On the other hand, it has been shown that the type of magnetism (spin glass, mixed antiferromagnetism-ferromagnetism) and therefore, the magnetic susceptibility of Cu-Mn films is strongly dependent on the temperature of deposition and annealing.[4] Similar effects of metallurgical treatment (quenching, aging, and cold working) have been seen on bulk Cu-Mn alloys.[5,6] Since the cusp is smallest in the deformed samples[5,6] and in films deposited at 77 K,[4,6] both procedures leading to a more random distribution of Mn atoms, this raises the question whether a cusp would exist in a totally random spin glass. This question could be answered by investigating the magnetic susceptibility of an amorphous spin glass because in such a system the spins are expected to be random in both direction (spin glass) and position (amorphous).

Although a cusplike peak in the magnetic susceptibility has been reported in two amorphous spin glasses,[7,8] these studies do not examine the structure sensitiveness of the cusp. In other words, the cusp was not studied as a function of recrystallization and some clustering of Gd atoms could have been present in both alloys: in the dilute $La_{80-x}Gd_xAu_{20}$ ($x \leq 0.7$) alloy because this amorphous alloy was obtained by liquid quenching and in $Gd_{0.37}Al_{0.63}$ because of the high Gd concentration.

An alloy system which seems particularly suited for the present study is the ternary alloy $Au_{0.81-x}Mn_xSi_{0.19}$. In the absence of Si, this ternary alloy becomes the well studied Au-Mn spin glass[3] while $Au_{0.81}Si_{0.19}$ is a well-established glass[9] (the word glass used here by itself refers to the amorphous state obtained by quenching a liquid). Furthermore, the electrical and structural properties of amorphous Au-Si (a-Au-Si) films have been recently reported.[10] Although Au-Si and Au-Mn-Si films are deposited at 77 K, they remain amorphous at room temperature and recrystallize close to 373 K, thus allowing a convenient study of the effects of annealing on the susceptibility cusp.

II. EXPERIMENTAL PROCEDURE

Since the experimental procedure is identical to the one described for a-Au-Si films,[10] it will be only briefly discussed here. The films were getter sputtered at 2.25 W (1500 V, 1.5 mA) with an argon pressure of about 3×10^{-2} Torr onto sapphire substrates held at 77 K. The sputtering targets were prepared by melting inductively[11] in an alumina crucible under an argon atmosphere the required amount of gold, silicon, and manganese. The manganese concentration which varied between 2 and 10 at.% was checked by x-ray fluorescence analysis. The film thickness was determined from the weight gain using as a density a linear average of the densities of the constituent elements. Any error in the film thickness resulting from such a determination is immaterial to the present study as the films are essentially bulk: the film thickness ranged from 12 to 25 μm. The amorphous nature of the films was ascertained by an x-ray diffraction trace and by differential thermal analysis (DTA).[12] For DTA the films were scraped off from the sapphire substrate with a razor blade.

TABLE I. Magnetic properties of a-$Au_{0.81-x}Mn_xSi_{0.19}$.

Sample[a]	Sample state	Rate (Å/min)	d (μm)	R	T_m (K)	Θ (K)		P_{eff} (μ_B)
0.02 No. 1	As deposited	90	13	1.3	6.5	•••		•••
	Ann. 293 K			1.4	7 (8.3)[b]	0(−1.5)	8.2	(10.6)
	Ann. 373 K			2.3	8.5	−2.5	•••	14.5
0.02 No. 2	As deposited	118	17	1.6	6.5	•••	•••	•••
	Ann. 293 K			1.8	6.5	•••	•••	•••
	Ann. 373 K			3.2	10	•••	•••	•••
0.05 No. 1	Ann. 293 K	100	25	1.7	18(17)	5 (7)	7.4	(11.5)
	Ann. 293 K[c]			•••	•••	13		5.7
	Ann. 373 K			3.9	26	8		28
	Ann. 423 K			9	28	8		29
	Ann. 473 K			6	28	8		29
	Ann. 573 K			5	28	8		29
	Ann. 573 K[c]			1.3	18	10		10
0.05 No. 2	Ann. 293 K	131	15	2.1	13	0		8
	Ann. 373 K			9.3	22	5.5		24
	Ann. 573 K			4.8	20	•••	•••	•••
0.05 No. 3	As deposited	93	13	1.5	14	•••	•••	•••
	Ann. 293 K			1.9	13	•••	•••	•••
	Ann. 423 K			9.3	28	•••	•••	•••
	Ann. 473 K			7.8	26	•••	•••	•••
0.10 No. 1	As deposited	96	14	2.9	24	•••	•••	•••
	Ann. 293 K			3	28(29)	•••	•••	•••
	Ann. 373 K			5.2	38	•••	•••	•••
0.10 No. 2	As deposited	120	17	2.4	28	•••	•••	•••

[a] Concentrations listed in this column refer to Mn, i.e., to the value of x.
[b] Values in parentheses are the corresponding values for Au-Mn from Ref. 3.
[c] Measured by the Faraday method with 1.4 kOe.

Following deposition the film is transferred under liquid nitrogen onto the push-rod susceptibility holder,[13] which is then immersed in liquid helium. The susceptibility of the film is then measured at 10 kHz with a modulating field of 4 Oe in helium gas as a function of temperature by warming to room temperature. For the high-field susceptibility measurement the sample was warmed to room temperature and scraped with fused quartz. The resulting powder was then placed in an ultrapure quartz container and measured by the Faraday method[14] at increasing temperatures after zero-field cooling.

The annealing of all films was performed by heating in a furnace under argon atmosphere except for the anneal at 1223 K where hydrogen was used. The annealing time at 293 K was 16 h.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic properties of a-$Au_{0.81-x}Mn_xSi_{0.19}$ films are summarized in Table I. As evident from Table I, the major portion of the study was conducted on the 5-at. % Mn composition and susceptibility curves for this composition are shown in Fig. 1 as a function of temperature. There are three salient points of interest to be discussed in conjunction with the data shown in Fig. 1.

First the susceptibility and the susceptibility peak [as measured by the ratio $R=\chi_{max}/\chi(4.2\text{ K})$] are smallest for the film as-deposited at 77 K. The susceptibility is about an order of magnitude lower than that reported for crystalline $Au_{0.95}Mn_{0.05}$ [$\chi(5\text{ K})=1.4\times10^{-4}$ emu/g][3] and R is 1.5 as compared to about 4 for crystalline $Au_{0.95}Mn_{0.05}$. Sec-

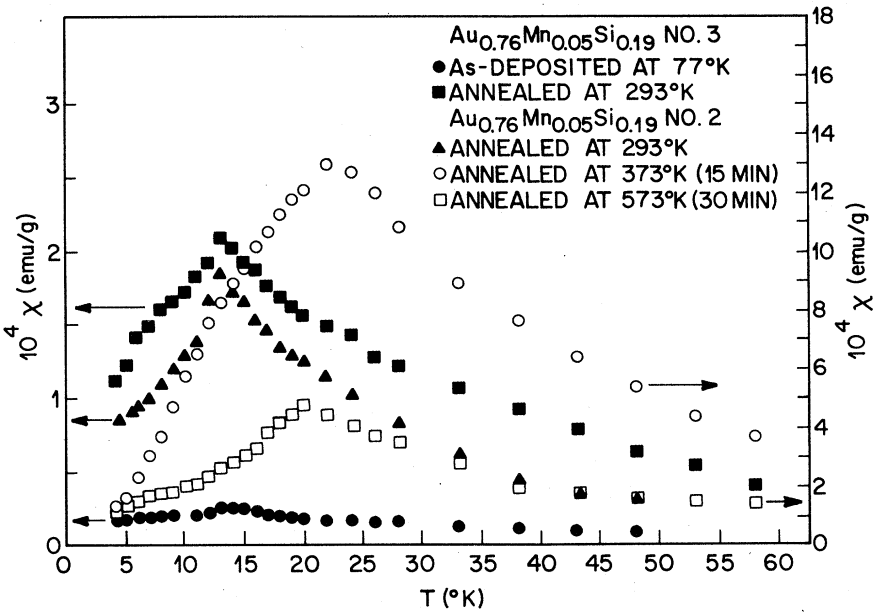

FIG. 1. Magnetic susceptibility vs temperature for $Au_{0.76}Mn_{0.05}Si_{0.19}$ films annealed at various temperatures.

ond, annealing the films at 293 K (which leaves the films amorphous as shown by the fact that the x-ray diffraction pattern for both Au-Si and Au-Mn-Si remains essentially unchanged[10] up to 373 K) increases χ by a factor of 5 and R to about 2 leaving T_m (the temperature corresponding to χ_{max}) essentially unchanged. Third, the most striking effect is observed after annealing at 373 K which increases both R and T_m to values exceeding crystalline Au-Mn results. Annealing to higher temperatures (above 423 K) leads to a reduction of R with little change in T_m. A quick perusal of Table I convinces one that these three effects are quite reproducible from film to film (compare the data for the three 0.05 Mn samples) and can also be observed for other Mn concentrations (0.02 and 0.10). It would therefore seem that these effects are fairly independent of Mn concentration.

Although it is known[1-3] that the susceptibility peak becomes both smeared and shifted by the application of a large magnetic field, it is clear from Fig. 2 that the effects discussed above are still observable in high field. The susceptibility peak at 4.3 kOe is smeared into a plateau for the sample annealed at 293 K but it is clearly present for both 1.4 and 4.3 kOe fields in the sample annealed at 573 K. It is also evident from Fig. 2 that there is a large increase in χ (especially in the temperature range of the peak) as a result of the 573 K anneal. Furthermore, the values of χ_{max} for the high-field data of Fig. 2 are only slightly lower (as expected[3]) than the corresponding values of χ_{max} shown in Fig. 1 for the low-field measurements.

Besides the values of R and T_m, the values of Θ (where Θ is the intercept $\chi^{-1}=0$ of a χ^{-1} vs T plot) and p_{eff} as obtained from a plot of χ^{-1} vs $T-\Theta$ are listed for a few cases in Table I and compared with bulk values.[3] The errors in the

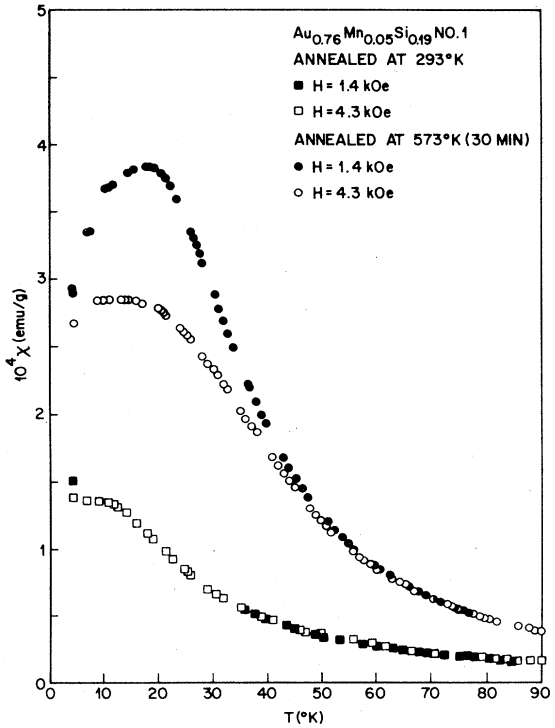

FIG. 2. High-field magnetic susceptibility measured by the Faraday method as a function of temperature.

measurement of Θ and p_{eff} are large as a consequence of the scatter in the high-temperature data shown in Fig. 1. This scatter results from the fact that the susceptibility is small when measured on a film and smallest at high temperature. The only conclusion that one can draw is that p_{eff} seems to increase as a result of annealing which suggests some clustering effects which shall be discussed later on.

In order to understand the annealing behavior of the susceptibility, there are three possible effects which come to mind: mean-free path, recrystallization, and some form of atomic rearrangement which may include short-range order or microclustering. It will now be shown that the first two effects most probably do not represent the correct explanation. First of all, as theoretically the interaction between spins is either of the Ruderman-Kittel-Kasuya-Yosida type[15] or most importantly is random (i.e., that different interactions via different paths between two spins should be competing[16]) one does not expect a mean-free path effect at least as long as the mean-free path does not get down to atomic dimensions. The resistivity (ρ) of the as-deposited 5-at.% Mn film is 90 $\mu\Omega$cm, using a ρl for pure Au of 1.2×10^{-11} cm^2,[17] the mean-free path l is equal to 13 Å. Since l is larger than the average Mn separation (about 8 Å using a Au interatomic distance[18] of 2.884 Å), one does not expect a mean-free-path effect. The fact that l is unimportant is even more convincingly established by the annealing at 293 K. While such annealing leaves ρ and therefore l rigorously unchanged, one can see from both Fig. 1 and Table I that χ and R increase substantially.

Similarly one does not expect theoretically crystalization to have a marked effect on χ and R but only on θ.[19] Indeed while θ_{cryst} can be greater or less than zero, $\theta_{amorphous}=0$.[15,19,20] Although as shown in Table I, $\theta=0$ in two amorphous cases, $\theta\neq0$ in one case but that, as discussed above, could be the result of the poor accuracy in the θ measurements of the present study. Again crystallization could be ruled out on the basis of the 293 K anneal which leaves the films amorphous[10]

TABLE II. Annealing properties of $Au_{0.76}Mn_{0.05}Si_{0.19}$ No. 2 (15 μm).

Annealing temperature (K)	Annealing time (min)	Resistivity ($\mu\Omega$cm)	Au(111) line (Hz)
293	960	90	0
373	15	86	0
423	15	43	100
473	15	26	140
573	30	25	1300

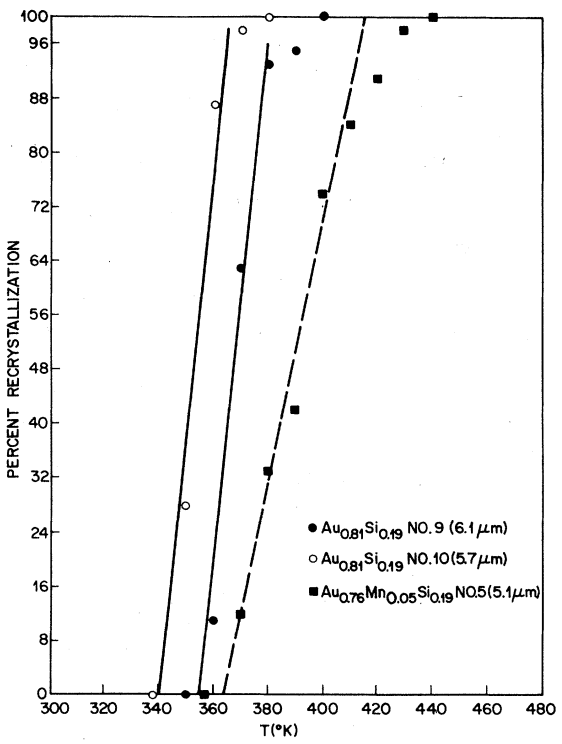

FIG. 3. Percentage recrystallization measured by differential thermal analysis as a function of annealing temperature.

but leads to substantial increases in both χ and R. However, as the major changes in χ and R occur upon annealing at 373 K and although no sign of crystallinity could be observed by x-ray diffraction,[10] one may worry about the presence of microcrystallinity which could remain undetected by x rays. This is why it is important to examine the crystallization of Au-Si-Mn alloys in more details. This is first accomplished in Table II where the resistivity and appearance of the Au(111) line are measured as a function of annealing. It is clear from Table II, that while complete crystallization at 573 K [the (111) line reaches its maximum value of 1300 Hz] results in a four-fold decrease in the resistivity, no sign of crystallization is visible at 373 K which is supported by the fact that the resistivity only decreased by 4%.

Crystallization has also been studied by[12] DTA and the results are shown in Fig. 3. The following conclusions can be drawn from the data shown in Fig. 3: although the crystallization temperature (T_{cryst}) can vary by about 20 K from sample to sample, Au-Si films are amorphous at room temperature and recrystallize over a temperature range of 20 K at $T_{cryst}\simeq350\pm10$ K. The absence of crystallinity at 373 K as seen by x rays[10] implies that a sufficient amount of grain growth is neces-

sary ($\simeq 423$ K) before crystallinity can be detected by x rays. The higher T_{cryst} observed in films as compared to bulk glass[9] (290 K) is most probably due to the small amount of argon (1 at.%) incorporated in the films. However, except for this difference in T_{cryst} the DTA revealed that the films are quite similar to the Au-Si glass[9]: one can observe the melting of the γ phase at 632 K followed by its crystallization and finally the melting of the eutectic at 643 K (these melting points are within 10 K of those reported for the bulk Au-Si glass[9]). Furthermore, the heat of crystallization of the Au-Si films (1450 cal/gfw) is in excellent agreement with that measured on the glass[9] (1426 ± 100 cal/gfw). The similarity between amorphous films and bulk glasses which has been recently suggested on the basis of resistivity[10] and x-ray experiments[10,21] is therefore further supported by the DTA.

The influence of Mn on the crystallization of *a*-Au-Si films reveals itself in two ways. As shown in Fig. 3 the onset of crystallization is slightly higher ($T_{cryst} \simeq 365$ K) and the crystallization takes place over a much wider temperature range ($\simeq 60$ K). It is noteworthy that this difference in crystallization behavior resulting from Mn is also associated with a difference in the mechanical properties of the film: while the *a*-Au-Si films could be scraped off with great ease, *a*-Au-Si-Mn films showed much greater hardness and adherence and could only be scraped off with great difficulty. At any rate, it is clear from the DTA data shown in Fig. 3 in agreement with the resistivity and x-ray data listed in Table II, that only a small fraction ($\simeq 20\%$) of the film is recrystallized at 373 K. This confirms the above statement that crystallization is not responsible for the annealing effects on χ and R observed at 373 K.

The annealing effects will now be examined in the light of the third mechanism: some form of atomic rearrangement. It will be assumed that, whatever atomic rearrangement takes place upon annealing, the as-deposited film at 77 K represents the most random state of the alloy. This assumption is supported by the fact that a minimal amount of atomic diffusion is expected at 77 K and by the more distorted x-ray pattern for the as-deposited film.[10] The atomic rearrangement which will now be considered[22] depends crucially on the presence of Si. In the crystalline fully annealed Au-Mn spin glass, a Mn atom is always surrounded by Au atoms and consequently, the crystal-field splitting is small compared to the exchange integral. The Mn is therefore in a $\frac{5}{2}$ spin state and the magnetism (qualitatively speaking) is proportional to $\frac{5}{2} \times \frac{7}{2} = \frac{35}{4}$. On the other hand, is the as-deposited *a*-Au-Si-Mn film, one can expect on a pure statistical basis that many Mn atoms will be surrounded by both Au and Si atoms. The presence of the Si atom will cause the crystal-field splitting to be large compared to the exchange integral and as a result the Mn will now be in a $\frac{1}{2}$ spin state. The magnetism is now proportional to $\frac{3}{2} \times \frac{1}{2} = \frac{3}{4}$ and is therefore much smaller than in the bulk glass. One is then led to assume that upon annealing an atomic rearrangement takes place such that the Si and Mn atoms tend to surround themselves with Au atoms. This assumption is supported by the tendence for such chemical ordering, Si surrounded by Au and Ge surrounded by Pd, inferred, respectively, from susceptibility[23] and extended x-ray absorption fine structure[21] (EXAFS) measurements. Therefore, as a result of annealing more Mn atoms become surrounded by Au atoms only, leaving the Si atoms in a Au-Si matrix which explains the increase in both χ and R. The increase of T_m with annealing results also from the increasing number of high spin state Mn atoms and is similar to the increase of T_m observed in the crystalline alloy[3] with increasing Mn content. One should also point out that although recrystallization *per se* is not the mechanism, the large annealing effects observed at 373 K must be linked to the fact that this temperature corresponds to the onset of appreciable atomic motion.

The above explanation based on Si atom redistribtion is certainly not a complete one because similar annealing effects can be observed in the absence of Si as shown in Fig. 4 and Table III. The data shown in Fig. 4 and Table III were obtained on Au-Mn films deposited in an identical manner to the *a*-Au-Si-Mn films, but because of the absence of Si, the Au-Mn films are crystalline and possess a low resistivity (13 $\mu\Omega$ m) even in the as-deposited state. Consequently, recrystalliza-

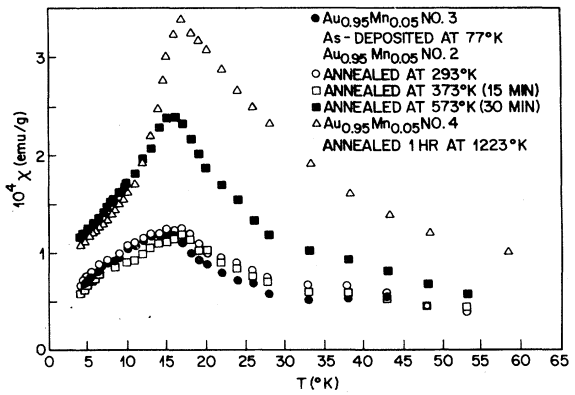

FIG. 4. Magnetic susceptibility vs temperature for various $Au_{0.95}Mn_{0.05}$ films annealed at different temperatures.

TABLE III. Magnetic properties of $Au_{0.95}Mn_{0.05}$ films.

Sample	Sample state	Rate (Å/min)	d (μm)	R	T_m (K)	Θ (K)	P_{eff} (μ_B)
No. 2	Ann. 293 K	86	12	1.8	16	...	...
	Ann. 373 K			2	17	...	...
	Ann. 573 K			2.1	16	4	9.7
	Ann. 823 K			2.6	16	...	...
No. 3	As deposited	165	24	1.8	16	4	6.6
No. 4	Ann. 293 K	146	19	1.9	16	5	6.8
	Ann. 1223 K			3.2	17	4	12.8

tion and mean-free-path (92 Å) effects are totally immaterial to the present experiments. Nevertheless, the annealing experiments shown in Fig. 4 for the Au-Mn films are very similar to those shown in Fig. 1 for a-Au-Si-Mn films. Indeed, both χ and R for as-deposited Au-Mn films are lower than for the fully annealed crystalline alloy[3] and both increase appreciably with annealing. There are however, three important differences with regard to a-Au-Si-Mn films: First, the annealing effects are smaller; second, T_m remains essentially unchanged by annealing, and third, the annealing effects occur at higher temperatures. The third difference is not a real one; although similar annealing effects occur at different temperatures they do occur at approximately the same homologous temperature (ratio of the temperature to the melting point). The homologous temperature to 373 K for $Au_{0.76}Mn_{0.05}Si_{0.19}$ which melts at 643 K is 767 K for $Au_{0.95}Mn_{0.5}$ which melts at 1323 K. As one may expect the same atomic mobility at the same homologous temperature one would predict that the appreciable annealing effects which occur at 373 K in a-$Au_{0.76}Mn_{0.05}Si_{0.19}$ should occur in $Au_{0.95}Mn_{0.05}$ at about 767 K which is confirmed by the data shown in Fig. 4. The other two different behaviors are undoubtedly connected with the presence or absence of Si atoms. It is not possible to explain how these differences arise as the annealing behavior of the Au-Mn films is not understood on a microscopic level. It is most probably safe to postulate that the annealing behavior of Au-Mn films is related to some departure from randomness of the Mn atoms: either some form of short-range order or of microclustering. The annealing effects observed in a-Au-Si-Mn at 293 K, which is below the onset of crystallization (and therefore of Si atom motion), are most probably similar in nature to those observed in Au-Mn films because χ and R increase while T_m remains unchanged (Fig. 1 and Table I).

IV. SUMMARY

The effects of annealing on the susceptibility and on the susceptibility peak of a-Au-Si-Mn films have been linked to some departure from randomness of both the Si and Mn atoms. This atomic redistribution (whether by short-range order or by microclustering) must require very small atomic displacements, since these changes can occur while the films remain mostly amorphous. It is planned to further study the nature of these atomic rearrangements by EXAFS analysis. These experiments also suggest that a susceptibility peak would be absent in a totally random amorphous alloy.

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