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FERROMAGNETIC AND ANTIFERROMAGNETIC COUPLING IN AMORPHOUS $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$

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W. M. KECK LABORATORY OF ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

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NOTICE

ABSTRACT

The magnetic properties of amorphous alloys $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$ with 0.7 at.% ≤ c ≤ 20 at.%, have been investigated for temperatures between 1.7°K and 270°K. Samples were prepared by the splat cooling method; the susceptibilities at zero field and the magnetizations in fields up to 70 kOe have been measured. $Ni_{78}P_{14}B_8$ is paramagnetic and Ni-Mn-P-B alloys exhibit different magnetic characteristics depending on the manganese concentration and the temperature range. At "high temperature" T ≥ 30°K the initial susceptibility has a Curie-Weiss behaviour; all the paramagnetic Curie temperatures θ are equal to zero or positive. The low temperature studies show that three concentration regimes can be determined; i) for c ≤ 2 at.%, a dilute alloy behaviour is observed. For higher manganese concentrations the magnetization features show the existence of a mixing of ferromagnetic and antiferromagnetic coupling between atoms. ii) For 2 at.% < c ≤ 8 at.% the alloys present spin glass characteristics i.e. a random magnetic coupling occurs between magnetic moments. iii) For 8 at.% < c ≤ 20 at.% the alloys are mictomagnetic and show a trend toward an antiferromagnetic order; irreversible phenomena are observed. In this paper the experimental results are interpreted and discussed in relation with the spin glass and mictomagnetic models.

INTRODUCTION

Amorphous alloys of transition metals (Mn, Fe, Co, Ni) with metalloids (B, C, Si, P) exhibit several types of magnetic behaviours. For alloys containing one transition element magnetic properties are relatively simple to understand; Mn-P-C[1] was reported antiferromagnetic; Fe-P-B[2], Fe-P-C[3] and Co-P-B[4] are ferromagnetic, Ni-P-B[5] is paramagnetic although a trend toward a ferromagnetic transition is observed at high nickel concentration. In an amorphous alloy, when one transition element can be continuously substituted for another, a wide range of varying magnetic behaviours can be obtained. Magnetic properties of an Fe-Mn-P-B-Al[6] alloy exhibit irreversible phenomena which are interpreted as evidence for ferromagnetic-antiferromagnetic "exchange anisotropy". Fe-Mn-P-C[1] exhibits a transition from ferromagnetism to antiferromagnetism when the manganese concentration is increased. Studies on Ni-Co-P-B[4] alloys show the existence of a paramagnetic-ferromagnetic transition which can be understood in the same way as in crystalline concentrated alloys and compounds.

In this paper we study the magnetic properties of $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$ amorphous alloys with $0.7 \leq c \leq 20$ at.% Mn. In this study we are mainly interested in the magnetic behaviour of an isolated manganese atom and the characteristics of interactions between magnetic atoms when the manganese concentration is increased. We show that for $c \lesssim 2$ at.% Mn, Ni-Mn-P-B has a dilute alloy behaviour; for higher manganese concentrations, the magnetic properties can be understood

by the coexistence of ferromagnetic and antiferromagnetic coupling between magnetic atoms, these properties can be compared in some way with those observed in spin glass and mictomagnetic crystalline alloys. In order to do such a comparison and since definitions depend on the authors, let us review briefly what is meant by spin glass and mictomagnetism in crystalline alloys like Cu-Mn[7,8,9], Au-Fe[10], Mo-Fe[11], which are characterized by the existence of long range interactions between magnetic impurities. Such a definition was first proposed in reference 10: at low concentrations of the transition element Mn or Fe, where interactions are negligible the concentration range is called dilute regime. In the spin glass regime the impurity concentrations were such that the magnetic properties are mainly determined by the long range interactions. In the mictomagnetic concentration regime the magnetic properties are related to both long range and short range interactions between magnetic impurities.

EXPERIMENTAL PROCEDURE

Foils of $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$ were obtained by quenching from the liquid state using the "piston and anvil" technique, full details of the alloys preparation can be found in reference 12; the concentrations given in this paper are nominal. The X-ray diffraction spectrum of each foil was checked with a Norelco diffractometer. These spectra showed that in the amorphous state manganese can be substituted for nickel for concentrations up to 20 at.% Mn. The variations of zero field susceptibilities were determined by an induction method using an ac bridge; the investigated temperature range was included between 1.7K and 270K. The

magnetization measurements were performed by the Faraday method using an Oxford Instrument magnetometer described in reference 13; the magnetic field was varied between 0 and 70 kOe and the temperature between 1.7 and 270K.

EXPERIMENTAL RESULTS AND DISCUSSION

For manganese concentrations between 2 at.% and 8 at.% the zero field susceptibility S exhibits a cusp at a temperature T_M. This temperature T_M varies linearly with c at a rate of about 1K/at.% Mn (Fig. 1); extrapolation of the T_M vs c curve shows that if an S cusp exists for $c \leq 2$ at.% it occurs below the investigated temperature range. For $c \geq 10$ at.% no S cusp was detected; this could be due to a large decrease of the cusp magnitude when c is increased, as observed in Cu-Mn alloy.[8]

For all the investigated samples the initial susceptibility χ_o varies according to a Curie-Weiss law $\chi_o = C_{cw}/(T + \theta)$, over a wide temperature range. For instance for c = 20 at.% Mn, deviations from this law occur at $T \ll 30$ k and for lower c such deviations are observed at lower temperatures. The paramagnetic Curie temperatures θ are all equal to zero or positive ($0 \leq \theta \leq 6$ K). θ increases with c until a concentration of about 8 at.% Mn, then it decreases smoothly with c (Fig. 1). The Curie constant increases linearly for $c \leq 2$ at.%, then saturates progressively. The effective moment per manganese atom, determined from C is constant for $c \leq 2$ at.% Mn, then it decreases from $5.9\mu_B$ to $4.3\mu_B$. Amorphous alloys with $c \geq 5$ at.% Mn exhibit a maximum of the initial susceptibility at a temperature close to that

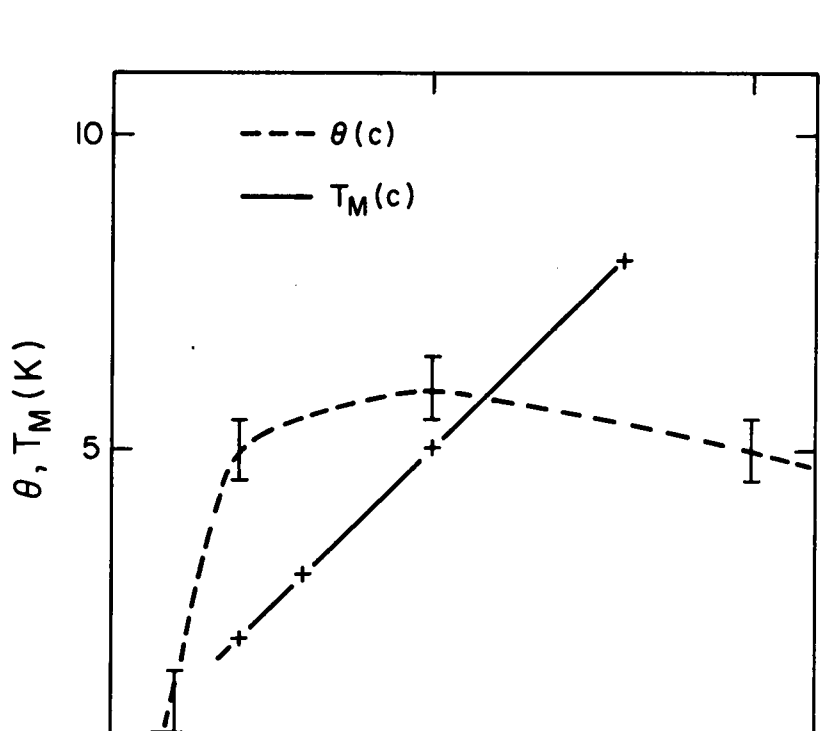

Fig. 1. $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$: variation of the "ordering temperature" T_M and the paramagnetic Curie temperature θ as a function of manganese concentration.

of the S cusp, when such a cusp exists; for samples for which no cusp is detected, a rather broad maximum is observed at a temperature which is increasing with c.

At low temperature $T \lesssim 30$ K, the magnetization M(H, T) shows a continuous approach to saturation with increasing magnetic field. However this saturation approach becomes slower when the manganese concentration is increased. At constant field and temperature, M(H, T) as a function of c increases until about 8 at.% Mn, then it decreases smoothly (Fig. 2).

For $c \geq 8$ at.% Mn, irreversible magnetic phenomena are observed below T_M or below the maximum of the susceptibility χ_o. For the sample containing 5 at.% Mn our measurements show that such phenomena exist but their magnitude is very small compared to the total magnetization and could not be determined accurately. At a given temperature, for a sample cooled at zero magnetic field, the first magnetization curve exhibits roughly an S shape; it starts increasing linearly with H until $H \simeq 3$ kOe then it has a postive curvature and finally becomes concave downward at high field $H \gtrsim 7$ kOe. At decreasing field, the magnetization curve is concave downward. If the magnetic field is again increased, the magnetization curve is linear in a rather wide field range ($H \lesssim$ kOE) then it is concave downward (Fig. 3). As a result M(H, T) exhibits an hysteresis loop comparable to those observed in antiferromagnetic alloys, after applying a high magnetic field. When the alloy is cooled in a constant magnetic field, the magnetization increases until T_M then it is constant below T_M.

The previous experimental results on $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$, in particular the initial susceptibility maxima, the variation of the mag-

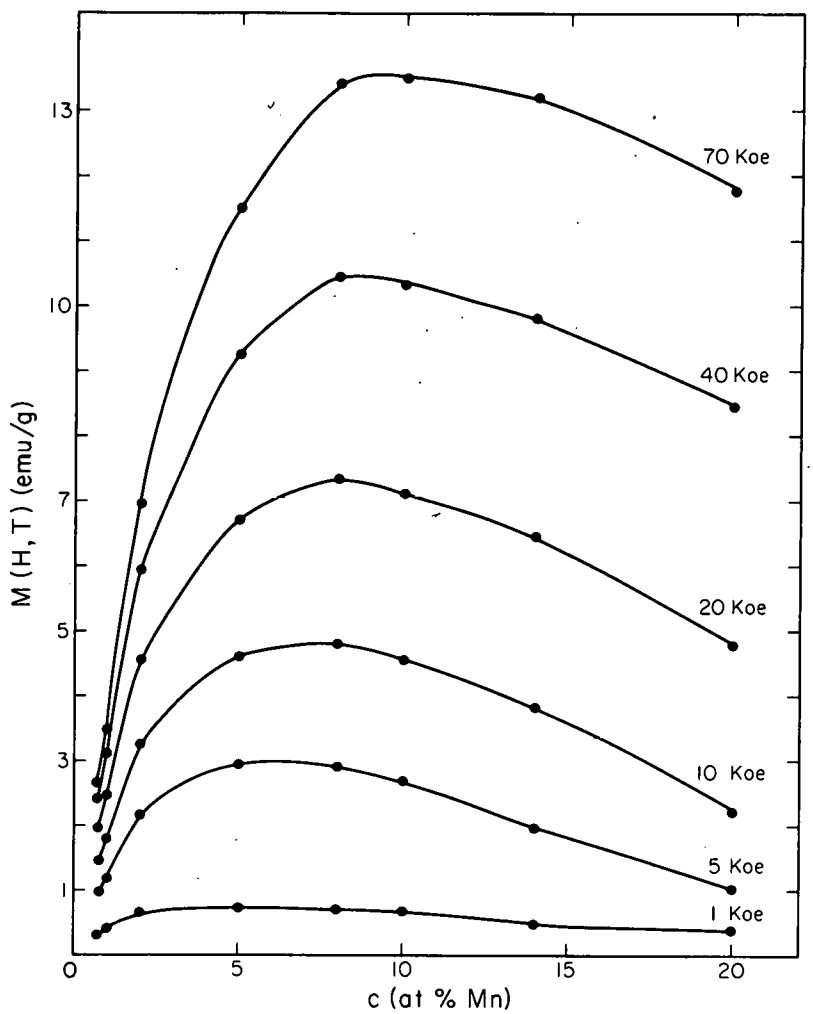

Fig. 2. $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$, T = 1.7K: variation of the magnetization with manganese concentration, at constant field, for alloys cooled at zero field.

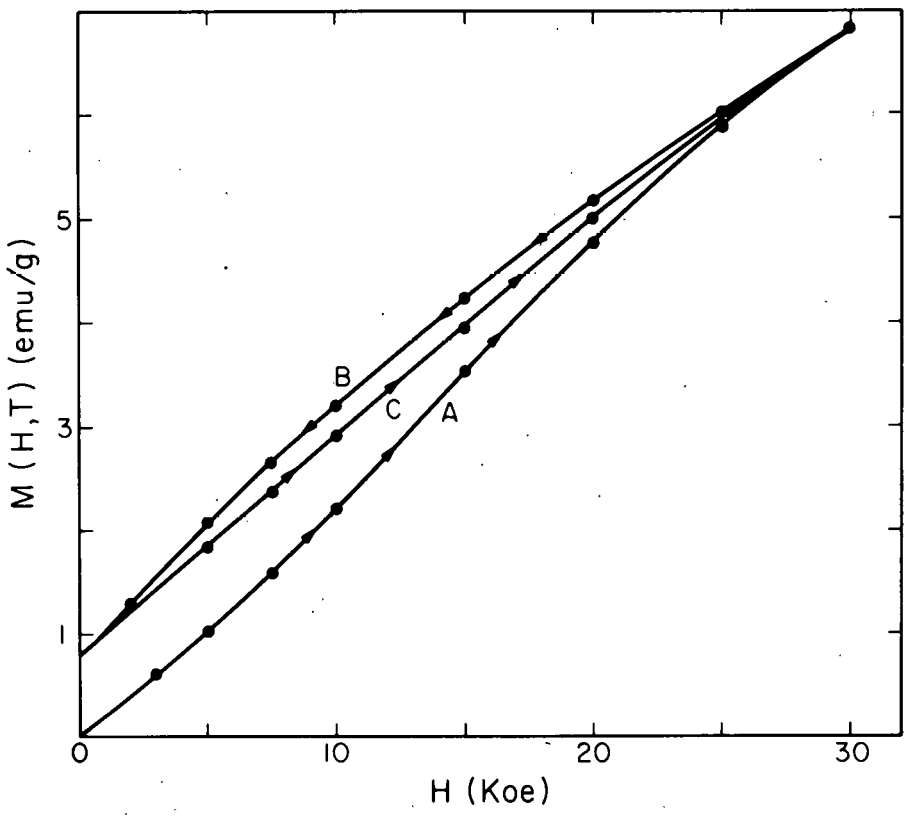

Fig. 3. $(Ni_{80}Mn_{20})_{78}P_{14}B_8$ T = 1.7K alloy cooled at zero field: magnetization M(H, T) vs magnetic field.

A: first magnetization curve
B: magnetization at decreasing field
C: magnetization at increasing field

netization as a function of c and H, show the coexistence of a ferromagnetic and an antiferromagnetic coupling between magnetic atoms. The small values of the paramagnetic Curie temperature may be related to the structure of amorphous alloys. It has been previously suggested[14] that the near zero θ values obtained in the amorphous state are due to the fluctuations of the interatomic distances. From our experimental results we can roughly determine three manganese concentration ranges: a dilute regime $c \lesssim 2$ at.% where the manganese atoms behave as isolated atoms; a spin glass like regime 2 at.% $\lesssim c \lesssim$ 8 at.% where a random magnetic coupling occurs between magnetic moments and finally a mictomagnetic regime $c \geq 8$ at.% where a trend toward an antiferromagnetic order occurs. However let us note that this separation expresses only the fact that a certain type of magnetic characteristics is predominant in a given regime; the transition from one regime to another is not abrupt but progressive, therefore the boundary between them is only approximately defined. In the following we discuss in more detail the magnetic characteristics of each concentration regime.

Dilute regime $c \leq 2$ at.% Mn: In this concentration range C_{cw} and M(H, T), at a given temperature and magnetic field, are increasing linearly with manganese concentration; for c = 2 at.% some departure from the dilute behaviour is observed at 1.7°K (Fig. 4); this can be attributed to the occurrence of magnetic interaction below 4.2°K. Previous studies on Mn-Pd-Si[15] amorphous alloys showed a limit of the dilute regime at about 1.5 at.% Mn. The effective moment per manganese atom determined from C_{cw} is 5.9μ_B; this value is close to those obtained in Mn-Pd-Si.[15] However at low temperatures the magnetization cannot be described by a single impurity contribution and the

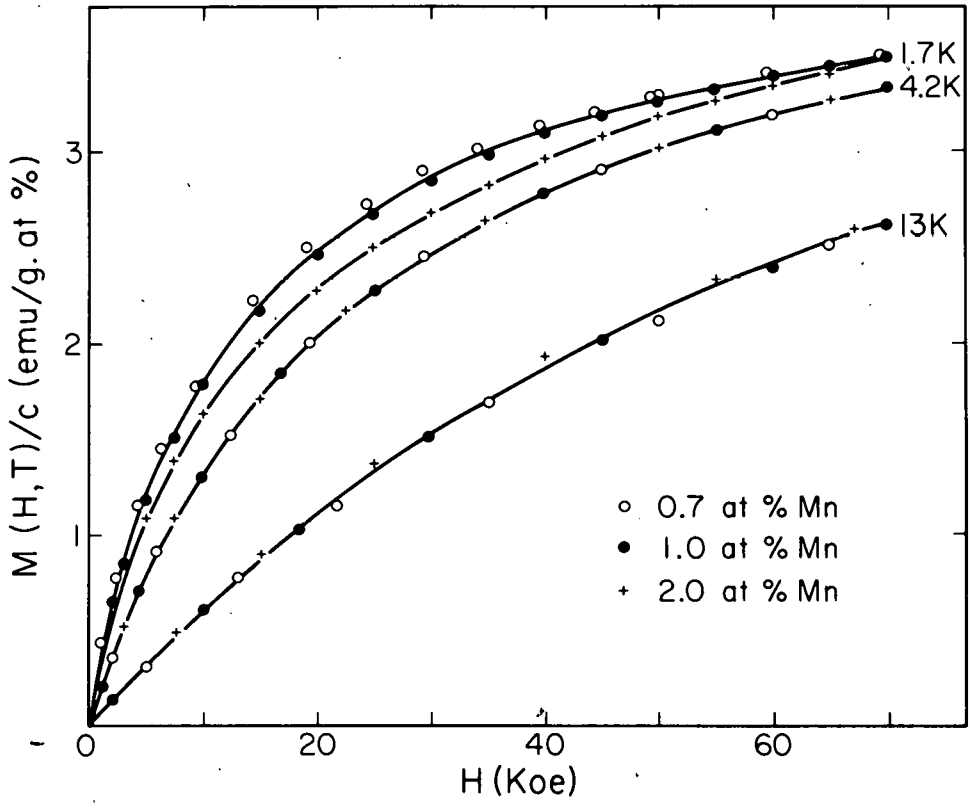

Fig. 4. $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$: magnetization per impurity M(H, T)/c as a function of magnetic field, for low manganese concentration.

moment deduced from the saturation magnetization is only about $3\mu_B$. These features may be attributed to a polarization of nickel atoms surrounding the manganese atoms.

Spin glass like regime 2 at.% ≤ c ≤ 8 at.% Mn: in this concentration range, as mentioned previously, the zero field susceptibility exhibits a cusp at T_M and M(H, T) is increasing with c. Moreover for 3 at.% ≤ c ≤ 7 at.% the magnetization at low temperature is varying roughly according to a scaling law (Fig. 5) i.e.: the magnetization per manganese impurity M(H, T)/c is a unique function of the reduced variables H/c and T/c. These experimental features suggest the occurrence of a randomly distributed ferromagnetic and antiferromagnetic coupling between manganese atoms. In crystalline alloys such as Cu-Mn[7, 8, 9], and Mo-Fe a similar behaviour has been observed, and some theoretical models[16, 17, 18, 19] have been proposed to account for the experimental results. The cusp of the zero field susceptibility is attributed to the occurrence, below T_M, of a magnetic ordering where the impurity moments are frozen in randomly distributed directions; this ordering arises from an oscillating interaction between magnetic moments. Assuming a RKKY interaction[17, 18, 20], it has been shown that the magnetization and the specific heat are varying according to a scaling law. However recent NMR results on CuMn[9] suggest that the interpretation of a cooperative freezing involving all the moments at T_M, is questionable. Such a process would be rather progressive with decreasing temperature, although an important freezing occurs at T_M. On the other hand for Ni-Mn-P-B amorphous alloys if we assume that a transition atom is surrounded by an average of 12 transition atoms, as suggested by structural studies[20], the spin glass properties occur

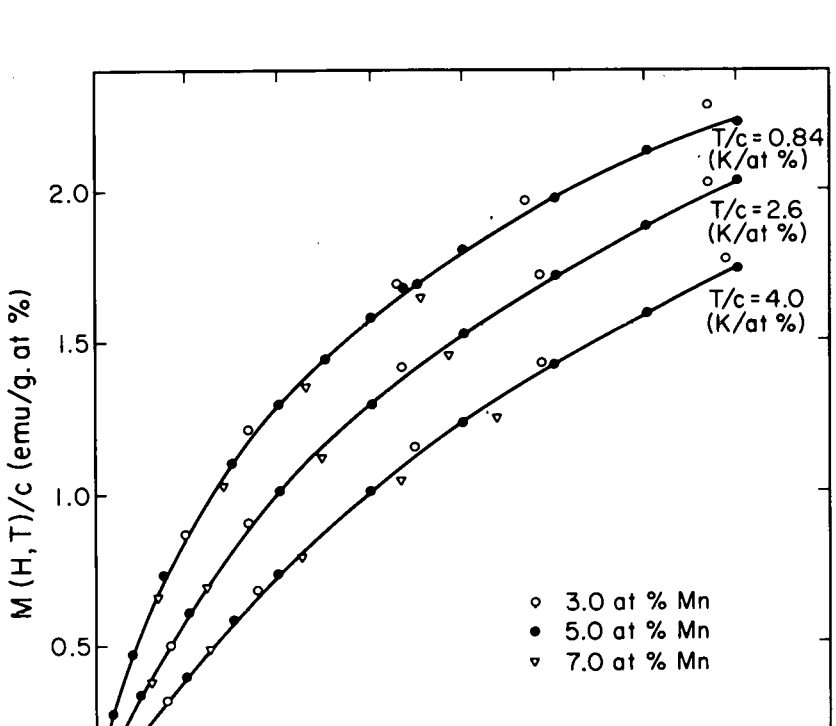

Fig. 5. $(Ni_{100-c}Mn_c)_{78}P_{14}B_8$: magnetization per impurity M(H, T)/c as a function of H/c and T/c (scaling law).

in a concentration range where cluster effects cannot be neglected. As a matter of fact for these concentrations, the probability of having pairs, triplets etc.---of manganese first neighbors is large. Therefore the magnetic properties of Ni-Mn-P-B cannot be unambiguously related to long range interactions of RKKY type. The origin of ferromagnetic and antiferromagnetic coupling may also be due to a short range effect; it may be related to the existence, for a given manganese atom, of neighboring manganese atoms at various distances; thus the nature of the magnetic coupling may depend on the distance between magnetic moments.

Mictomagnetic regimes c > 8 at.%: In this concentration range, at a given low temperature ($T \lesssim 30^{\circ}K$) and magnetic field, the magnetization is smoothly decreasing with increasing c. This shows that antiferromagnetic coupling is becoming predominant as the manganese clusters become larger in the alloy. The low field measurements show that, for a sample cooled at zero field, the initial susceptibility deduced from M(H, T), measured at increasing field, is independent from any field previously applied. The high field magnetization shows the persistence of a strong antiferromagnetic coupling between magnetic atoms; for instance at 20 at.% Mn, the average magnetization is about $0.68\mu_B$ per manganese atom. The constant susceptibility and the characteristics of the irreversible effects suggest, as in Au-Fe[10] and Mo-Fe[11] alloys, the formation below the χ_o maximum, of magnetic domains of which resulting moments are interacting. When the alloy is cooled in zero field these resulting moments are progressively frozen in random directions. When a small magnetic field H is applied these directions are not affected; at a higher field the domains are oriented in the H direction. When the alloy is cooled in a magnetic field the resultant

moments freeze in a preferential direction which is that of the applied field. A further study of the irreversible effect, especially the remanant magnetizations and the hysteresis loop, should provide more details on the domains and the origin of their coupling.

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