# Magnetic Structures in Reentrant Spin-Glasses Observed by Transmission Electron Microscopy

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Direct observations of the magnetization structure in two reentrant spin-glass alloys [polycrystalline $Ni_{1-x}Mn_x$ and amorphous $(Fe_{78}Mn_{22})_{75}P_{16}B_6Al_3$] near liquid-helium temperature are reported. Magnetic domains several hundred $\mu$m long are seen. This structure hardly changes upon cooling through the reentrant transition ($T_f \simeq 35$ K). *In situ* observation of the domain-wall motions reveals a gradual crossover to a regime of strong irreversibilities. Reentrant spin-glass systems are also characterized by transverse fluctuations within the domain.

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Many crystalline and amorphous alloys with a random mixture of ferromagnetic and antiferromagnetic interactions undergo a paramagnetic-ferromagnetic-like transition at a certain temperature $T_c$, but at a lower temperature $T_f$ the ferromagnetism seems to disappear giving rise to a spin-glass-like or reentrant state. During the last decade, reentrant spin-glass (R-SG) transition has been extensively investigated both theoretically and experimentally by means of many different techniques, including not only global magnetic measurements but also other methods probing the magnetic structure on microscopic scales. The most common of these are small-angle neutron-scattering experiments[1-4] (few hundred angstroms), transport measurements[5] (scale of the electron mean free path $\simeq 5$ to 50 Å), and Mössbauer spectroscopy[6] (atomic scale).

However, up to now, the complexity of the R-SG problem has made it very difficult to interpret the experimental data unambiguously, so that the exact nature of the reentrant transition is still unclear and highly controversial. Some of the debated questions are as follows: (1) What is the structure of the magnetization in the so-called ferromagnetic phase[7] ($T_f \leq T \leq T_c$)? (2) What then happens to it in the reentrant phase (i.e., for $T < T_f$)? (3) What are the physical origins of the field and temperature dependences of the global magnetization $m(T,H)$ near and below $T_f$?

In particular, does the well-known sudden drop of the zero-field-cooled magnetization $m_{ZFC}(T)$ below $T_f$ correspond to the vanishing of the spontaneous magnetization and consequently to a well-defined phase transition as has often been claimed? In an effort to clarify this situation we have carried out direct investigations of the domain structure by means of Lorentz transmission electron microscopy[8]. Three representative R-SG alloys [polycrystalline $Ni_{1-x}Mn_x$ with $x = 0.15$, 0.19, 0.21, and 0.25, amorphous $(Fe_{78}Mn_{22})_{75}P_{16}B_6Al_3$, and amorphous $Fe_{90}Zr_{10}$] were examined as functions of temperature ($10 \leq T \leq 290$ K) and field ($0 \leq H \leq 1$ kOe). Because of the lack of space the results on the FeZr alloy will be reported elsewhere.

Two different instruments were used in this investigation, the high-voltage transmission electron microscope of the Laboratoire d'Optique Electronique du Centre National de la Recherche Scientifique de Toulouse (operated at 2 MV) and a Philips model EM400 (biased at 120 kV) equipped with a field-effect filament. Each of the two instruments is provided with a helium-cooled sample holder, the temperature of which could be controlled within a few degrees from $\simeq 10$ to 290 K. To avoid perturbing the domain structure the microscopes were generally used with the objective lens switched off, except for the study of the domain-wall motion where small fields were needed. The residual field within the microscope is of order 10 Oe. This field is expected to have little influence on the observed magnetic structure both because it is perpendicular to the film plane and because of the associated large demagnetizing factor which leads to a very low internal field ($H_{int} \simeq H + H_d \leq 10^{-2}$ Oe). One of the advantages of high-voltage transmission electron microscopy is the wide range of specimen thicknesses, up to 1 $\mu$m (bulk limit), that can be investigated. Several other interesting features and advantages of the two apparatus will be described elsewhere, together with other experimental details.

Figure 1 shows a typical example of magnetic structure at $T = 12$ K in a foil of $Ni_{81}Mn_{19}$ prepared by electropolishing. The alternating dark and light traces represent domain walls or domain barriers. To study the possible influences of structural defects and Mn concentration, we also investigated the domain structure both in foils thinned by the ion-beam technique and in 1000- to

 


FIG. 1. Domain-wall images (dark and bright lines) at 12 K for electropolished $Ni_{81}Mn_{19}$.

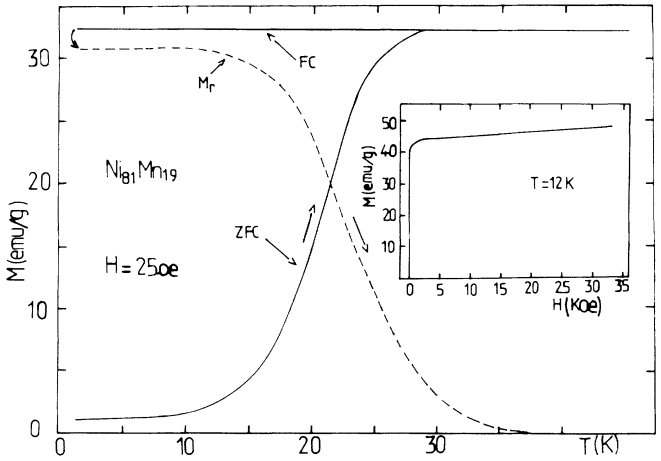


FIG. 2. Temperature variation of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations of $Ni_{81}Mn_{19}$ as in Fig. 1. Inset: High-field behavior of $m_{ZFC}$ at $\simeq 12$ K.

4000-Å sputtered films of $Ni_{1-x}Mn_x$ at various concentrations and temperatures. The same typical domain networks as in Fig. 1 were generally observed though the domain configurations were often severely obscured by structural defects and oxidation. The most significant conclusions reached from the above systematic investigations can be summarized as follows.

The newest result to be emphasized is of course the existence of a well defined, "macroscopic," domain structure well below $T_f$ ($T_f \simeq 35$ K). A second fundamental observation is the fact that the domain structure and the associated magnetic contrast appear to be exactly the same (within the precision of the eyes) in the reentrant and in the ferromagnetic phases. The third important data is the "macroscopic" size of the domains, some of which are as large as 10 $\mu$m and as long as several hundred microns. It was indeed seen that in some films the domains extended over the whole film from one side to the next. A fourth characteristic feature concerns the approximately linear shape of the domain walls and therefore the role of magnetocrystalline anisotropy in the NiMn system.

To help the discussion of the nature of the reentrant phase we have also carried out standard magnetic measurements. These are illustrated in Fig. 2, which shows the temperature dependence of both the field-cooled [$m_{FC}(T)$] and the zero-field-cooled [$m_{ZFC}(T)$] magnetizations of $Ni_{81}Mn_{19}$. Having in mind the domain structure in the zero-field-cooled state (Fig. 1), it is now obvious that the drop of $m_{ZFC}(T)$ (for $T \leq T_f \simeq 35$ K) has nothing to do with the disappearance of the spontaneous magnetization but is certainly connected with the onset of a regime of strong coercivity and anisotropy forces upon cooling through the reentrant phase.[9] The inset in Fig. 2 presents the magnetic cycle ($m$-$H$ curve) in field up to 35 kOe. The most interesting feature of this cycle is the lack of magnetic saturation and thus the persistence of a large differential susceptibility up to the highest field available. This is, of course, the signature that a large degree of spin disorder ($\approx 40\%$ in the present case) persists even in the monodomain state well above the technical saturation limit. At this point, it is interesting to note that magnetoresistance measurements[5] on similar NiMn alloys show that such "spin-glass-like" disorder coexists with ferromagnetic order on a microscopic scale of the order of the electron mean free path ($\simeq 5$ to 50 Å). It is also interesting to emphasize that small-angle neutron-scattering experiments[1-4] indicate static-spin fluctuations on the scale of 100 to 500 Å.

Figure 3 displays an example of magnetic structure in a thin film ($\simeq 1000$ Å) of amorphous $(Fe_{78}Mn_{22})_{75}P_{16}B_6Al_3$ at about 14 K. It is to be noted that the canting temperature of the same sputtered films deduced from an EPR study[10] is about 80 K, whereas the R-SG transition deduced from the $m$-$H$ curves (Fig. 4 and Ref. 9) is about 35 K. As in the case of the NiMn system, we found that the domain network is essentially the same on either side of the reentrant phase. The principal difference with respect to NiMn concerns the geometry of the domain walls which are now curved.

Figure 4 shows the temperature dependence of the magnetic cycle and the coercive field of the same specimen as in Fig. 3. We note a rapid increase of the coercivity effects below $T_f \simeq 35$ K. To facilitate and reinforce the analysis of the irreversibility effects reported just above, it would be interesting to get direct "visual" evidence of the reentrant transition. We have been able

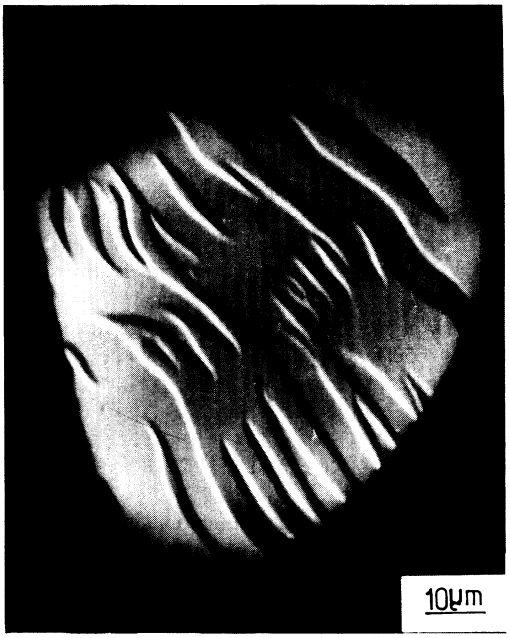


FIG. 3. An example of magnetic structure at 14 K in a film (1000 Å) of amorphous $(Fe_{78}Mn_{22})_{75}P_{16}B_6Al_3$.

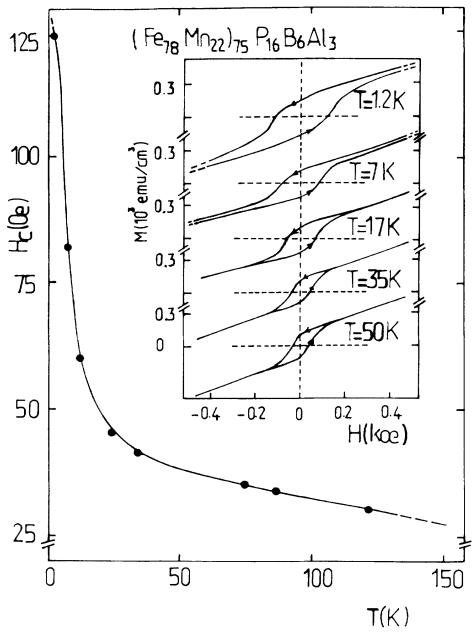


FIG. 4. Coercive field and hysteresis loops (inset) vs $T$ for $(Fe_{78}Mn_{22})_{75}P_{16}B_6Al_3$ film (1000 Å).

to obtain such information by studying the evolution of the domain-wall motions as well as viscosity and time aftereffects within the microscope as functions of $T$ and $H$. The most typical results are as follows.

The response time of the domain structure (i.e., the time taken to reach a steady state) after a steplike variation of $H$ (1 kOe$\rightarrow$ 0) is very fast (approximately equal to the time constant of the instrument, a few seconds) over the whole ferromagnetic phase, but it increases sharply below 30 K exceeding 300 s at about 15 K. It is of interest to note that this time scale is comparable to the time decay of the remanent magnetization ($m_r$) in spin-glasses, suggesting that the usual decay of $m_r$ is not a homogeneous process but is more probably a nucleation propagation process at different parts of the sample.

To make further comparison with global magnetic data we have also carried out "visual" measurements of the in-plane field above which the film becomes a single domain. We found that this threshold field is roughly constant ($\approx$45 Oe)[11] in the temperature range 40–250 K but increases markedly at lower temperatures, reaching 150 Oe at $\simeq$15 K, in reasonable agreement with the magnetic measurements of Fig. 4 and Ref. 9.

The picture that emerges from the present semimicroscopic observations as well as from global magnetic[9] and transport[5] measurements and from low-angle neutron-scattering experiments[1-4,12] is that the R-SG alloys are characterized by successive organizations of the magnetization over a very extended spatial scale. First of all, there are long-range ferromagnetic correlations limited only by the finite size of the ferromagneticlike domains. The spatial structure of the latter is itself imposed by the classical trade-off between magnetostatic self-energy on the one hand and exchange energy together with magnetic (magnetocrystalline, magnetoelastic, or shape) anisotropy energies on the other hand. Strikingly enough, the usual spin-glass parameters such as frustration and positional disorder which have been often invoked to explain the macroscopic properties of the reentrant phase do not seem to play any significant role at these large spatial scales.

Second, there is evidence from the above data that the magnetization within the domain themselves is not uniform but presents a large degree ($\simeq$40% in the present cases) of static or frozen fluctuations. A third important feature of the present work is the confirmation that two of the most typical properties of the reentrant phase [i.e., the shape of the magnetic cycle and the drop of $m_{ZFC}(T)$ below $T_f$] are certainly connected with the onset of strong coercivity and anisotropy forces upon cooling through the reentrant phase.

The various effects reported in this Letter are not easy to understand on the basis of the existing mean-field theories for R-SG alloys. More fundamentally, it seems that these phenomena cannot be accounted for accurately within the framework of the standard Sherrington-Kirkpatrick Hamiltonian[13] alone. Dipolar as well as anisotropic-exchange interactions[9,14] are probably also needed to explain the experimental data. Finally, it

should be stressed that the present data do not support any of the superparamagnetic cluster models often discussed in the literature. We hope that the present observation will spur new theoretical efforts in this field.

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[7]This phase is referred to as ferromagnetic because it is characterized by a divergence of the ferromagnetic spin correlation length as deduced from neutron data (Refs. 1–4), by a divergence of the magnetic susceptibility $\chi$ (actually, as in conventional ferromagnets $\chi$ is limited by the reciprocal demagnetization factor $1/N$), and by an apparent saturation of the magnetization ($m_s$) in relatively low fields: $H_{\rm sat} \approx 10$ to 100 Oe. However, this phase is also marked by other less usual effects, one of which is the persistence [H. Rakoto, J. C. Ousset, S. Senoussi, and I. A. Campbell, J. Magn. Magn. Mater. **46**, 212 (1984)], after the apparent saturation $m_s$ mentioned just above, of a large spin-disorder term even in fields as high as 300 kOe. This is inferred both from a large negative magnetoresistance ($\simeq 50\%$ at 300 kOe) and from the absence of full magnetic saturation at these high fields.

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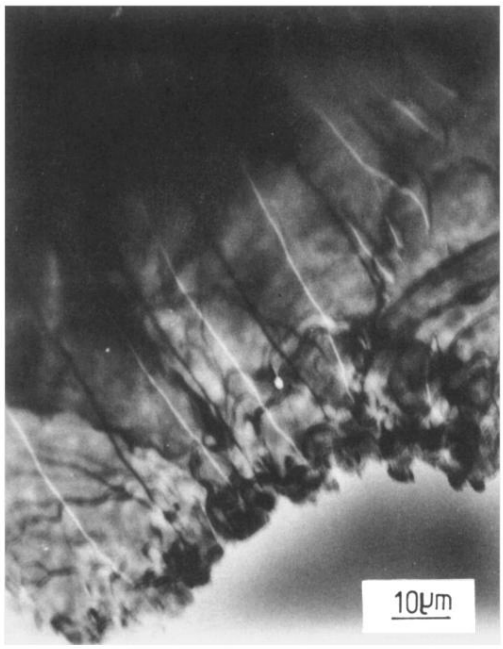


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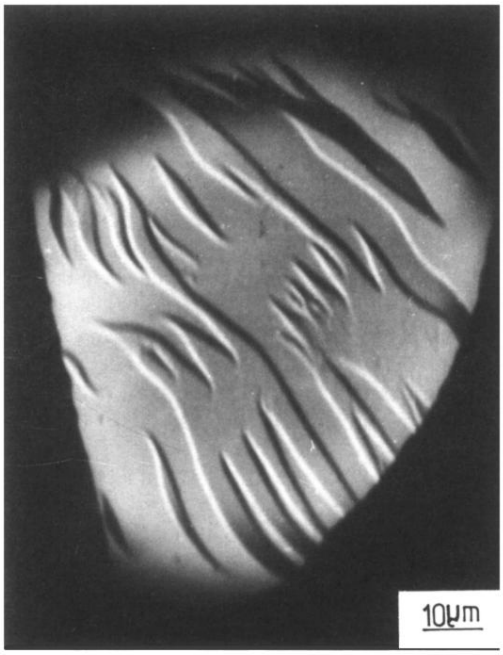


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