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1992 J. Phys.: Condens. Matter 4 7219

(http://iopscience.iop.org/0953-8984/4/35/007)

J. Phys.: Condens. Matter 4 (1992) 7219–7228. Printed in the UK

The low-field magnetoresistance properties of the re-entrant spin-glass system $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$

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Received 4 March 1992, in final form 15 May 1992

Abstract. The magnetoresistance (MR) of two re-entrant spin-glass (SG) alloys in $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ with $x = 9.1$ at.% and 11.36 at.% have been measured over the temperature range 4.2–300 K using a new ultra-sensitive MR apparatus enabling operation in magnetic fields comparable with that of the Earth. In this temperature range, the MR exhibits three distinct features: (i) a hysteresis effect over the whole so-called ferromagnetic (FM) region which generally saturates in only a few Gauss followed by reversible behaviour at higher fields; (ii) predominantly positive MR under low field conditions indicative of FM-type coupling between moments; but (iii) in the $x = 11.36$ at.% sample near the FM–paramagnetic (PM) and FM–SG boundaries, the MR changes sign in higher fields and becomes negative.

The results are discussed in terms of a recently proposed magnetic phase diagram for this system. The results support the existence of a mixed FM-like and SG phase but it is proposed that the 'FM' phase is mixed also with little or no long-range ferromagnetism. Instead, a system of FM-coupled clusters and a system of weakly coupled moments is indicated by the results, the latter behaving paramagnetically near the so-called Curie temperature but freezing into an SG state at lower temperatures.

1. Introduction

In this paper we report some new measurements of magnetoresistance (MR), performed in magnetic fields comparable with that of the Earth, on some re-entrant polycrystalline $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ alloys covering both the so-called paramagnetic–ferromagnetic (PM–FM) and ferromagnetic–spin-glass (FM–SG) transitions. Such FeNiMn alloys can exhibit paramagnetism, ferromagnetism, spin-glass and re-entrant spin-glass properties and antiferromagnetism depending on the value of x. The magnetic phase diagram of the FCC $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ system is shown in figure 1. Whilst, in general, MR is closely connected with the magnetization which exists in such alloys (this normally being proportional to the modulus of B, the magnetic induction raised to a power, n, where $n \sim 2$), it is, however, capable of providing more subtle information than say, straight magnetization measurements [1]. For example, as we have shown in a recent publication, [1], all normal spin-glasses (SGs) which we have studied are quite unambiguous in yielding an MR which peaks at the freezing temperature T_f *and* is always negative both in the paramagnetic and the frozen SG state. However, whenever ferromagnetism sets in, for example in the re-entrant SGs, the sign appears to be always positive. A particularly interesting case has been presented [1] in the case of Au-14 at.% Fe which when quenched exhibits classical SG behaviour with a negative MR, but simply annealing at room temperature for a few days results in a gradual sign change to positive as atomic redistribution to a re-entrant SG takes place. The sign of the magnetization, however, remains positive throughout this ageing process. In other words, MR, as well as responding to changes of magnetization, can also provide some information on the *type* of coupling between moments which exists in metallic magnetic systems. Thus we have been able to show [1], that in FeNi amorphous alloys ordinary PM or SG coupling appears to co-exist with a ferromagnetic-like phase within the so-called ferromagnetic phase, and continues to exist at and beyond the Curie temperature.

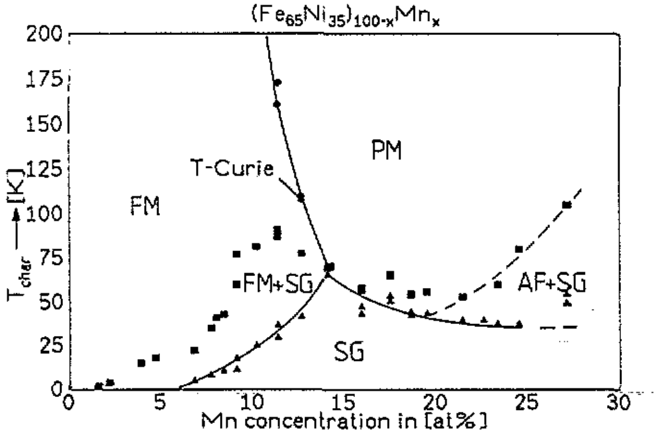

Figure 1. The magnetic phase diagram for the alloy system $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ redrawn after [6]. The measurements were performed in different magnetic fields using a Faraday balance and a SQUID magnetometer. These results for zero applied magnetic field were achieved by interpolation. ●, indicate the Curie temperature; ■, the maximum in the spontaneous magnetization; ▲, the transition temperature into the spin-glass state.

We have now extended our examination of re-entrant systems into the crystalline FeNiMn system where ostensibly a similar behaviour of the susceptibility exists to that of the amorphous FeNi system. However, in the MR there appears to be important differences in the 'ferromagnetic' (FM) region, including a very low field hysteresis but reversible behaviour at higher fields.

The MR was measured using a DC current (typically ~ 0.2A) through the alloy samples together with a magnetic field B in the direction of current flow. To achieve the very high sensitivity, the magnetic field was periodically switched on and off with a typical frequency in the range 40–90 Hz and the MR signal, also a square wave, fed to a high gain transformer and hence to a lock-in-amplifier. The MR is defined as the dimensionless ratio

$$\Delta\rho/\rho = (\rho(B) - \rho(0))/\rho(0) \tag{1}$$

where $\rho(B)$ and $\rho(0)$ are respectively the electrical resistivities with and without the magnetic field applied. The possibility of performing the MR measurements in vanishing magnetic fields has enabled us to operate under two separate modes. In one, the unidirectional square-wave pulses producing the magnetic field can be changed in magnitude and the corresponding MR measured, and in the other, differential method, a small square-wave field is used against a background variable DC magnetic field. The two schemes are depicted in figures 2(*a*) and (*b*), the latter case being particularly useful where hysteresis effects are encountered since it has enabled us to directly obtain coercivities, both in the SG and FM states. In this case the MR is defined as

$$\Delta\rho(B)/\rho(B) = (\rho(B+\Delta B) - \rho(B))/\rho(B) \quad (2)$$

where $\Delta(B)$ is the change in magnetic field as indicated in figure 2(*b*). In measuring hysteresis loops, the DC current and its flow direction through the sample remains constant as does ΔB. Only the magnetic field B is changed in the usual manner $0 \longrightarrow B_{max} \longrightarrow 0 \longrightarrow (-B_{max}) \longrightarrow 0$. Full details of the apparatus and method will be described elsewhere.

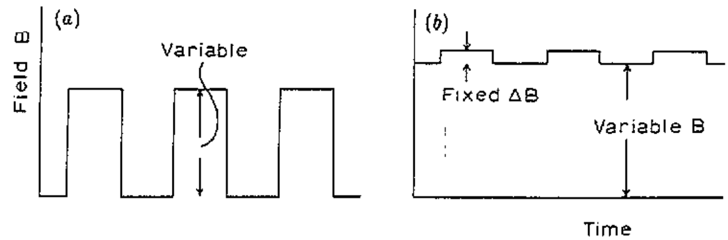

Figure 2. Schematic diagram showing two modes of operation of the AC MR apparatus. In (*a*) the magnitude of the pulsed square-wave field can be changed in magnitude and in (*b*) a small pulsed field is employed against a background variable DC field.

2. Sample preparation

The samples were prepared from $Fe_{0.65}Ni_{0.35}$ foils, 20μm thickness, supplied by Goodfellow Metals and the addition of Mn was achieved by a high-temperature diffusion process. Here particles of Mn and the FeNi foils were sealed in quartz under a vacuum of better than 10^{-2} bar, and annealed at 1300 K for a few hours. By this time the Mn had almost disappeared through diffusion into the foil. Further annealing for 120 hours was sufficient for homogenization followed by a rapid quench into iced water which preserved the disordered state. The Mn concentration was determined by weighing the foils before and after the diffusion process. Microprobe analysis showed good homogeneity although other experimental data suggested that near the foil edges slightly higher than average concentrations of Mn may be obtained leading to a lowering of the Curie temperature of these alloys. The alloys were also examined by x-ray diffraction which indicated that both samples were in the disordered FCC state and independent work on the same samples by synchrotron radiation showed no evidence of Mn clusters.

3. Results

The AC susceptibility and Mössbauer effect of these FeNiMn alloys have already been reported [2, 3]. In this work, samples from the same batch have been employed.

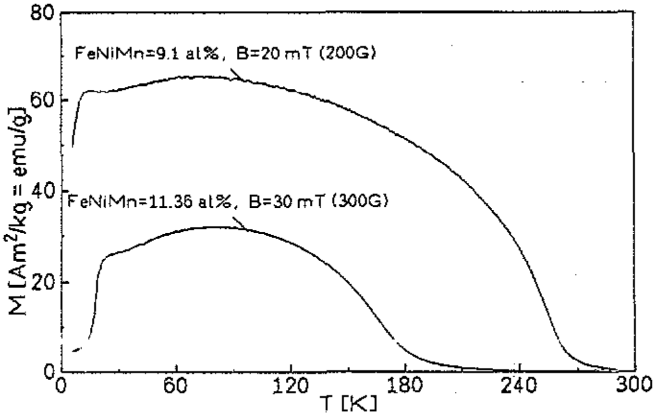

Figure 3. Magnetization versus temperature for $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ with x = 9.1 at.% and 11.36 at.% as measured with a Faraday balance. The applied magnetic fields are indicated.

Figure 3 shows magnetization measurements obtained from a Faraday balance for the alloys in question. It is evident that there is an enormous influence of small changes in Mn concentration on the magnetic properties such as the Curie temperature, maximum magnetization and re-entrant temperatures which, in the latter case, is indicated by the breakdown of the spontaneous magnetization at low temperatures. Typical AC susceptibility (ACS) results are shown in figure 4(*a*) for $x = 11.36$ at.% in which re-entrant behaviour is exhibited; i.e. for zero field a steep rise in the ACS occurs at the PM–FM transition temperature of 160 K and the typical 'knee' at lower temperatures indicative of the 'FM–SG' transition occurs. Of significant interest in these alloys, however, is the presence of local maxima in the ACS near the transition temperature when measurements are made with a small background magnetic field. Two of the maxima exhibited by the $x = 11.36$ at.% sample in a field of 20 G (figure 4(*b*)) have been carefully examined by low-field MR measurement and appear later in this paper.

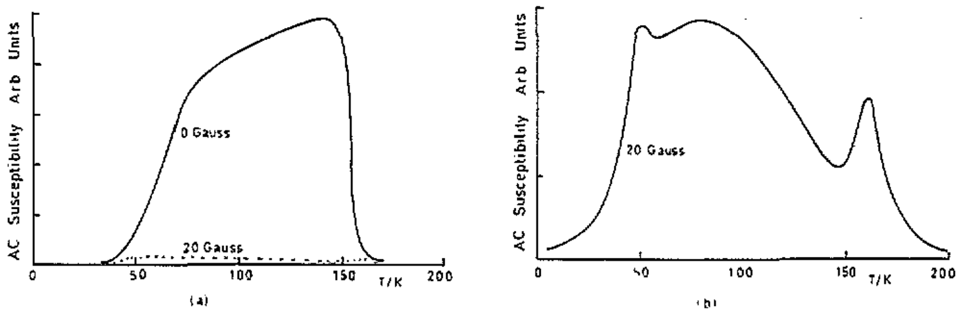

Figure 4. The AC susceptibility as a function of temperature for $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ with $x = 11.36$ at.% in (*a*) zero applied field, and (*b*) a field of 20 G.

The alloy with $x = 9.1$ at.% Mn is also a re-entrant SG with a Curie temperature T_C of approximately 250 K. At liquid nitrogen temperature the sample is in the 'FM' region and in figures 5 and 6 we show the measured MR at 78.35 K obtained by the two techniques described earlier. The outstanding feature of these variations is the very low-field hysteresis effect which occurs and the reversible behaviour at higher fields. In both cases very careful annulling of the Earth's field was necessary to obtain the symmetrical curves shown. We have used the differential MR curve (figure 6) to extract a coercivity value associated with the hysteresis which appears to saturate above about 10 Oe at this temperature. It should be noted that the MR is positive in this alloy as is clear from figure 5 for both positive and negative applied pulsed fields; the negative values obtained by the differential method (figure 6) occur as a result of the applied pulsed field (0.32 G) decreasing the magnetization, and hence the MR, induced by the negative DC field. In view of these unexpected results we have examined this behaviour over the temperature range 15–250 K which covers both the so-called SG and FM ranges. In figure 7 is shown the coercivity obtained by this technique as a function of temperature together with additional values obtained using a SQUID magnetometer ($B_{max} = 1000$ G). This shows a very steep rise as the mixed FM+SG state is entered as well as showing the hysteresis extending right up to T_C. Figure 8 shows a typical hysteresis curve in this region. It is to be noted that here, as at higher temperatures, reversible MR occurs at high applied fields and it is also significant in this alloy, that no negative MR has been observed down to 15 K, a feature generally associated with the SG state. A careful examination for negative MR at temperatures around the Curie temperature was also made in this alloy. Strong negative MR over a small temperature region about T_C was an important new feature which was reported in [1] in amorphous FeNi alloys just prior to the establishment of the 'FM' state, but this property was absent from this re-entrant sample in both zero static field and also in a background field of 9 G.

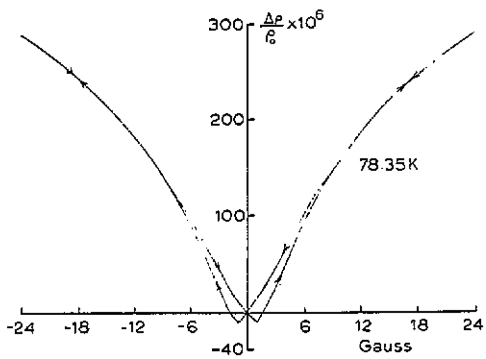

Figure 5. The variation of the MR at 78.38 K in $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ with $x = 9.1$ at.% as a function of the applied magnetic field of the form shown in figure 2(*a*).

We have not presented a complete MR versus T variation for this sample because the presence of the low-field hysteresis introduces ambiguity as to the precise magnetic state and hence the MR of the sample. However, in zero field, the MR versus T curve we obtained possessed a similar profile to that of the ACS shown for $x = 11.36$ at.% Mn in figure 4(*a*) reflecting the close connection between the MR and the modulus of the magnetization.

The addition of further Mn to FeNi reduces the Curie temperature and in the case of $x = 11.36$ at.% Mn, T_C is approximately 160 K. There was also much less hysteresis in the MR at 78 K so that it was possible to obtain meaningful MR versus T variations above this temperature free from the uncertainties of the magnetic state of the sample provided a sufficiently large excitation pulsed field was applied. In this sample we were particularly interested in the MR in the region of the peaks shown in

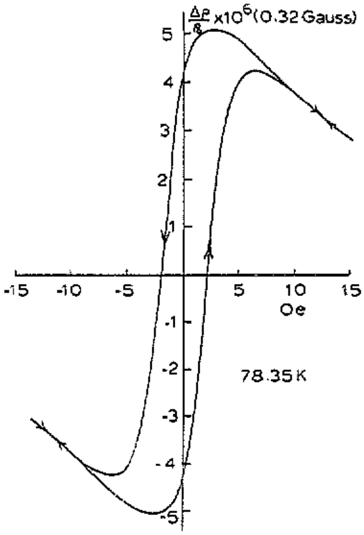

Figure 6. The variation of the differential MR in a 0.32 G field at 78.35 K in $(Fe_{0.65}Ni_{0.35})_{1-x}Mn_x$ with $x = 9.1$ at.% as a function of the variable field as shown in figure 2(*b*).

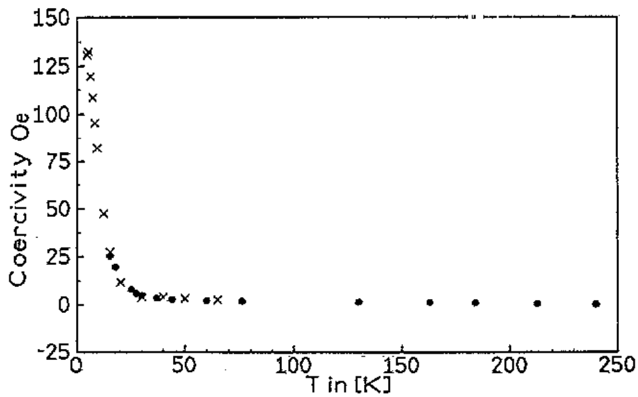

Figure 7. The coercivity of the $x = 9.1$ at.% sample as a function of temperature. ●, results obtained from the MR; ×, results from a SQUID magnetometer.

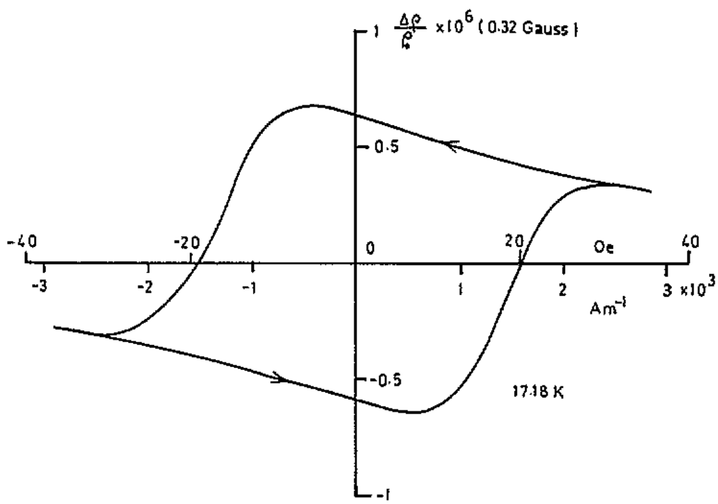

Figure 8. A typical magnetoresistance hysteresis curve for $x = 9.1$ at.% in the low temperature 'SG' region.

figure 4(*b*) where a biasing field of 20 G was applied. In figure 9 is shown a plot of MR versus T in the region around T_C taken in a peak field of 1.6 G with zero and 20 G biasing fields. In figure 10 we show the corresponding ACS of pieces of sample taken immediately adjacent to the MR sample, the measurements being performed under zero and 20 G fields also. It is apparent that the peak in the ACS at 150 K is matched by a similar peak in the negative MR which has developed as a result of the biasing field and is almost absent in zero biasing field. This sample therefore possesses the same characteristic negative MR near T_C observed in amorphous FeNi alloys [1] but here a biasing field is necessary to reveal it.

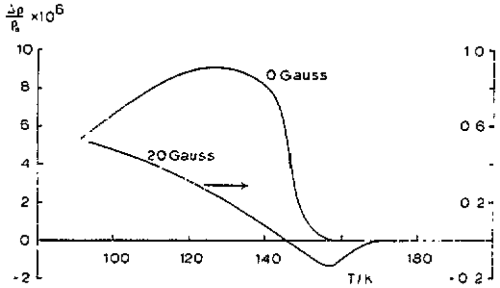

Figure 9. Magnetoresistance versus temperature in a pulsed field of 1.6 G for $x = 11.36$ at.% with biasing fields of 0 and 20 G in the temperature region near T_C.

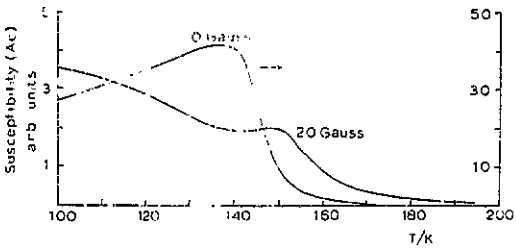

Figure 10. AC susceptibility of $x = 11.36$ at.% in 0 and 20 G fields near T_C.

A similar investigation of the MR in the region of the 'SG' transition (~ 55 K) also shows the establishment of a substantial negative MR which peaks at 44 K and a positive peak at ~ 90 K (figure 11) when under a field of 20 G. Again, the negative MR is absent under zero field and as figure 11 shows, no MR was observed below 55 K; above 55 K a large positive MR developed matching a similar steep rise in the ACS (figure 4(*a*)). It is thus clear that the two extreme peaks in the ACS shown in figure 4(*b*) are associated with the negative peaks shown in figures 9 and 11. This low-temperature behaviour is markedly different from that of $x = 9.1$ at.% Mn where no negative MR was observed in any field above 15 K. From figure 3 it is clear that the 9.1 at.% alloy is a much stronger ferromagnet than the 11.36 at.% sample, the maximum magnetization is double, the Curie temperature is about 240 K and the re-entrant temperature lies below 15 K (approximately 8 K).

In view of these unexpected and diverse results obtained in the MR of the 11.36 at.% sample, a more detailed examination of the field dependence was undertaken at temperatures in the vicinity of the negative peak and at 78 K. In figure 12 we show the MR at 78 K in three small pulsed fields as a function of the biasing DC field and in figure 13 the corresponding variations at 44.3, 47, 48, 49 and 50 K. At 78 K, again a very small hysteresis effect at low fields was observed similar to that in the $x = 9.1$ at.% Mn sample but with a lower coercivity; however, at the lower temperatures this type of behaviour changed dramatically over a very small temperature range, as shown in figure 13, in which the hysteresis vanished at 48 K then to reappear with solely negative MR and substantial coercivity at lower temperatures. Note that the vanishing of the hysteresis does not coincide with the temperature (40 K) of the negative peak in the MR at 20 G. It is clear that these very low-field MR measurements have yielded new and unusual phenomena taking place at the so-called SG transition.

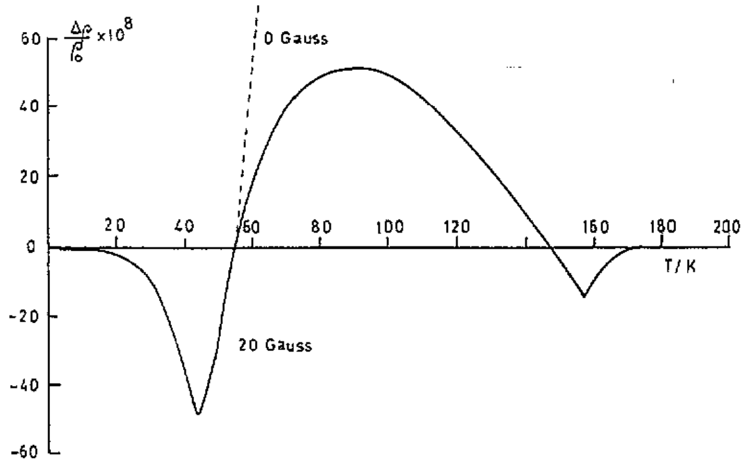

Figure 11. Magnetoresistance versus temperature for 11.36 at.% under a pulsed field of 1.6 G with biasing fields of 0 and 20 G in the vicinity of the so-called SG transition and near the Curie temperature. In 0 G (static) the MR was too small to measure below 55 K.

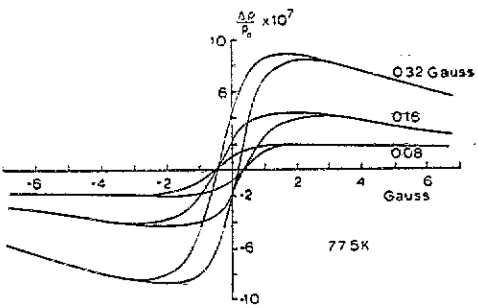

Figure 12. Magnetoresistance hysteresis curves for $x = 11.36$ at.% at 77.5 K in pulsed fields of 0.08, 0.16 and 0.32 G.

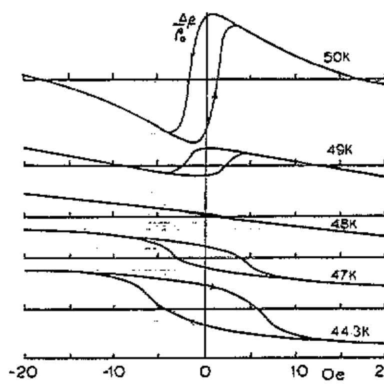

Figure 13. Magnetoresistance hysteresis curves for $x = 11.36$ at.% at 44.3, 47.0, 48.0, 49.0 and 50.0 K in a pulsed field of 3.2 G. In each case, the ordinate scale is the same.

4. Discussion

4.1. The high-temperature PM–FM transition and FM state

In zero field both the $x = 9.1$ and 11.36 at.% Mn samples, in contrast to the amorphous FeNi alloys presented in [1], show little or no evidence of negative MR developing at T_C. However, in an applied field of 20 G, the 11.36 at.% sample revealed a small negative component rather similar to those of the amorphous alloys. In [1] it was proposed that a dual type of magnetic coupling occurred, one of essentially FM-type yielding a positive MR and the other possibly of SG, or more likely, a PM-type giving negative MR. Such a similar explanation can be applied to the crystalline FeNiMn alloys with the FM component dominant at low biasing fields but at higher fields this component becomes locked-in and only the PM or SG component can then follow the pulsed MR field which reveals itself as a negative MR. Thus, this system supports our earlier suggestion that the so-called FM state contains PM or SG coupled moments also, or at least, two magnetic components. However, the existence of a low-field hysteresis effect in the 'FM' regime followed by reversible behaviour at higher fields appears to further complicate the interpretation of the FM state. Indeed, there is the suggestion that this state might comprise a further mixed system possibly with the saturateable component representing long-range ferromagnetism and another component of large FM-coupled clusters. This type of model can only be regarded as speculative, but clearly these MR results point to a much more complex magnetic structure than has hitherto been associated with the FM state in which PM or SG moments constitute an essential ingredient.

4.2. The low-temperature FM–SG tansition and the SG state

In the $x = 9.1$ at.% Mn sample, the coercivity undergoes a rapid rise in value as the temperature is reduced (figure 5) into the so-called FM+SG region. A similar rise in coercivity has been briefly reported by Miyazaki *et al* [4] in some amorphous FeNi alloys based on magnetization measurements; these authors have suggested that this may be a general characteristic of the re-entrant spin-glass state and may be explained by thermal activation of the wall-pinning model proposed by Gaunt and Roy [5]. This infers the existence of magnetic domains existing into the so-called FM+SG regime which may undergo size changes or canting as the SG state is entered. However, in the $x = 9.1$ at.% Mn sample, no negative MR has been observed here (at least down to 15 K) but examination of figure 8 strongly suggests that at high biasing fields the MR would become negative indicating that SG-coupled moments constitute part of the structure. On the other hand, in the 11.36 at.% Mn sample there is a clear establishment of solely negative MR below 48 K (figure 13) which is consistent with a transition to a purely SG state. Above 48 K both positive and negative MR is evident (see, for example, figure 13, 50 K) as in the 9.1 at.% Mn sample, suggestive of a mixed state possibly of FM and SG character. Such a mixed state has been proposed by some of us [6] in these alloys on the basis of magnetization measurements and a new magnetic phase diagram has recently been presented. Taking the 11.36 at.% Mn sample as an example, this alloy undergoes transitions from PM $\longrightarrow$ FM $\longrightarrow$ FM+SG $\longrightarrow$ SG as the temperature is lowered from 300 K. The FM+SG $\longrightarrow$ SG transition temperature, obtained from this new phase diagram, is approximately 40 K ($B = 0$), which compares reasonably well with the 48 K which we have found in this MR study. In the case of $x = 9.1$ at.% Mn, the same transition is at approximately 10 K, a temperature region we have not been able to fully cover in our MR work. Thus the MR measurements presented here strongly support this new magnetic phase diagram in which a mixed FM+SG phase is incorporated into the magnetic structure.

4.3. The so-called FM phase

As already mentioned, the existence of low-field hysteresis loops obtained from the differential MR measurements with reversible behaviour at higher biasing fields is not consistent with a pure long-range FM state. We are more inclined to the view repeatedly expounded by Rakers and Beck [7, 8] for re-entrant Au–Fe alloys in which the magnetization in the FM state is due to large ferromagnetic clusters and no long-range ferromagnetism. However, in the present alloys it is possible that the presence of low-field hysteresis may represent a small component of true FM imbedded in a matrix of large FM-coupled clusters or alternatively, a small percentage of pinned clusters exist giving rise to the hysteresis. In addition, we would also suggest that not all the moments are linked up with these clusters and a portion exhibit frustration thereby behaving paramagnetically at temperatures approaching T_C but undergoing an SG transition at lower temperatures. Such a model would certainly explain the presence of the small negative MRs observed near the Curie temperature which can only be seen when the positive MR of the clusters is rendered small by the randomization of magnetization from temperature and also blocked by the application of a biasing field. Likewise at low temperatures, the SG component is only observed when the positive MR component from the clusters to the AC MR is blocked by the application of a biasing field and by their presumed gradual breakup prior to the whole system entering the SG state at these lower temperatures. Thus the FM state is also mixed with FM clusters co-existing with a frozen SG state at lower temperatures and a PM state at temperatures approaching T_C.

5. Conclusions

By very low-field MR measurements, we have further investigated the magnetic phase diagram of two re-entrant FeNiMn alloys with concentrations of 9.1 and 11.36 at.% Mn. The results have yielded a new insight into the magnetic structure by virtue of the sensitivity of MR not only to the magnetization, but to the type of coupling which exists between the moments. We have also detected the presence of a low-field hysteresis effect in the MR of these alloys which we associate with either a small amount of long-range ferromagnetism or weakly pinned clusters in addition to a general matrix of large FM clusters. We also propose that some moments are sufficiently free to behave paramagnetically at high temperatures and SG-like at low temperatures leading to a non-simple mixed state of three components in the so-called FM state.

Acknowledgments

This work is supported by grants from the SERC (No GR/E/44901), the Salford Research Fund and the Deutsche Forschungsgemeinschaft Bonn–Bad Godesberg for which we would like to record our thanks.

References

[1] Barnard R D 1990 *J. Phys.: Condens. Matter* **2** 5191–8

[2] Huck B and Hesse J 1989 *J. Magn. Magn. Mater.* **78** 247–54

[3] Huck B, Landes J, Stasch R and Hesse J 1988 *J. Physique Coll. Suppl.* **49** C8 12

[4] Miyazaki T, Okamoto I, Ando Y and Takahashi M 1988 *J. Phys. F: Met. Phys.* **18** 1601–10

[5] Gaunt P and Roy G L 1976 *Phil. Mag.* **34** 781–8

[6] Wulfes A, Böttger Ch, Hesse J, Sievert J and Ahlers H 1992 *J. Magn. Magn. Mater.* **104–7** 2069–71

[7] Rakers L D and Beck P A 1987 *Phys. Rev.* B **36** 8622–8

[8] Rakers L D and Beck P A 1988 *Phys. Rev.* B **38** 7002–4