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Manifestation of a transition from a frustrated state to a ferromagnetic state in NiMn alloys: Resistivity minima

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We present low-temperature-resistivity measuremtents on five $Ni_{1-x}Mn_x$ alloys ($x = 0.21$, 0.25, 0.28, 0.30, and 0.33). Each alloy except $Ni_{0.79}Mn_{0.21}$ exhibits a resistivity minimum which we associate with the onset of a magnetic transition from a mixed (spin-glass plus ferromagnetic order) or frustrated state towards a ferromagnetic state. This interpretation is supported by magnetoresistance data.

The magnetic properties of disordered $Ni_{1-x}Mn_x$ alloys in the composition range 20- to 30-at.% Mn have been extensively studied during the past few years.[1–4] These properties are thought to be governed by long-range ferromagneticlike order below a critical concentration of about 25-at.% Mn and by spin-glass-like order at higher Mn content.[4] These conclusions have recently been confirmed by electron-spin-resonance measurements.[5] The composition 25-at.% Mn has also been investigated using both resistivity and neutron diffusion techniques.[6–8] Here we report, for the first time, measurements of the low-temperature resistivity $\rho(T)$ as a function of T for a range of concentrations extending from the ferromagneticlike regime to the spin-glass-like one. The interesting and unusual result (as far as spin-glass-like and ferromagneticlike alloys are concerned) is that (except for $x = 0.21$) $\rho(T)$ presents a deep minimum the shape and temperature of which strongly increases with concentration of maganese. To help in interpreting these findings we also carried out magnetoresistance measurements ($0 < 40$ kG and $1.2 < T < 80$ K) on $Ni_{0.72}Mn_{0.28}$ which was selected because it seemed to be usually considered as a very good example of a spin-glass alloy.

The most interesting result in this case is that the magnetoresistance varies as H^2 ($\Delta\rho/\rho_0 = -\beta H^2$) at 1.2 K (in the range of the available field < 40 kG) but approaches a linear behavior as a function of H near $T = 30$ K. Moreover, the $\Delta\rho/\rho_0$ vs T curve (in a fixed field) exhibits a very clear peak near this temperature.

The magnetic phase diagram of alloys such as $Ni_{1-x}Mn_x$ in the plane (x,T) has recently been investigated theoretically by Schlottmann and Bennemann.[9] Some interesting results of this investigation are the following: (a) No pure spin-glass state would exist in these alloys at any concentration. (b) For a certain range of concentrations the ground state would be a frustrated (or mixed) state with coesistence of both spin-glass-like and ferromagneticlike orders. (c) As the temperature is increased the mixed state would undergo a transition to a ferromagneticlike one which, in turn, would naturally be followed by a ferromagnetic-paramagnetic transition at higher T.

Now it is well known that the resistivity of a magnetic alloy is lower when the magnetic moments are locally aligned (on the scale of the electron mean free path) than when they are disaligned.[10] This fact then suggests that the anomaly in $\rho(T)$ reported here could reflect the emergence of a transition from an ordered to a disordered magnetic phase of the kind predicted in Ref. 9. It will be stressed, however, that according to the resistivity data such as transition would take place gradually as T is increased and this would not correspond to a true thermodynamic transition as currently predicted theoretically. We shall see later that other origins such as Kondo effects are quite improbable.

The specimens were prepared by melting together high-purity constituents in a rf furnace. To ensure a good homogenization each alloy was melted a minimum of three times and was further homogenized by cold working. Each sample was then rolled into an approximately rectangular plate ($\sim 15 \times 1.5 \times 0.08$ mm^3). Some of the specimens were first measured in their cold-worked states (i.e., immediately after the metallurgical treatment just described). After that, the specimen was encapsulated in a quartz tube (in vacuum) annealed ~ 4 h at 900°C and water quenched.

It was then kept in liquid nitrogen until transferred into the cryostat and measured using the standard ac four-points technique. Two of the samples ($x = 0.30$ and $x = 0.33$) were reannealed and remeasured using dc technique also. The ac and dc results were found to be the same within the experimental accuracy which was of the order of a few parts in 10^5.

Figure 1 shows the temperature variation of the resistivity $\rho(T)$ of our three less-concentrated alloys ($x = 0.21$, 0.25, and 0.28) in their annealed state. Concerning the $Ni_{0.72}Mn_{0.28}$ and $Ni_{0.75}Mn_{0.25}$ alloys we observe well-defined minima at around 7.5 and 3.5

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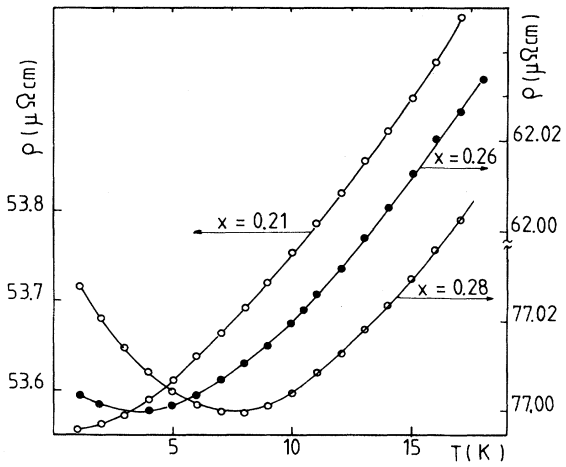

FIG. 1. Low-temperature-resistivity data on three annealed $Ni_{1-x}Mn_x$ alloys for $x = 0.21$, 0.25, and 0.28. Note the difference in the scales.

K, respectively. Contrasting with this behavior, the resistivity of $Ni_{0.79}Mn_{0.21}$ does not exhibit any minimum down to the lowest temperature of our measurements (1.2 K). Moreover, the change in $\rho(T)$ with T is much more rapid here than in the other cases as can be judged by comparing $d\rho/dT$ at 17 K (i.e., well above the temperatures of the minima) which are, for instance, equal to ~ 6 n Ω cm K^{-1} for $x = 0.28$ and ~ 45 n Ω cm K^{-1} for $x = 0.21$. In Fig. 2 we show how $\rho(T)$ depends upon T for $x = 0.30$ and $x = 0.33$. Here, too, we observe very well-defined minima which are deeper than at lower concentrations and take place at higher temperatures;

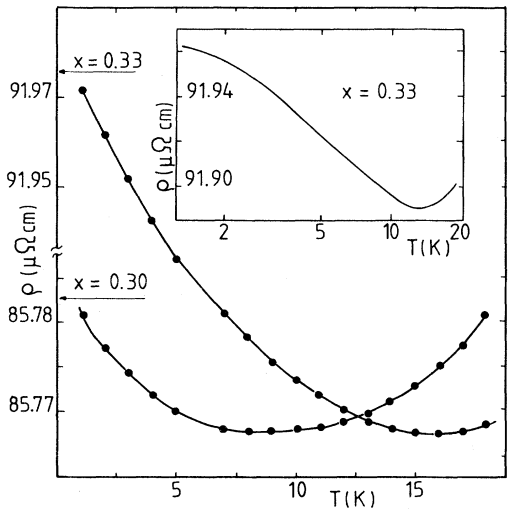

FIG. 2. Low-temperature-resistivity data on $Ni_{0.70}Mn_{0.30}$ and $Ni_{0.67}Mn_{0.33}$ (annealed). The resistivity of the same $Ni_{0.67}Mn_{0.33}$ sample is plotted in a semilogarithmic scale in the inset.

$T \sim 9.5$ K for $x = 0.30$ and ~ 15 K for $x = 0.33$. The inset represents a semilogarithmic plot of the resistivity associated with $Ni_{0.67}Mn_{0.33}$. Though it is hard to draw any definite conclusion from a result held over only about a temperature decade (1–10 K), the form of the curve in the inset does not seem to follow a logarithmic behavior.

The concentration dependence of both T_m and $\Delta\rho_m$ are presented in Fig. 3. The full curves are associated with the annealed samples, whereas the dashed one corresponds to the T_m associated with the same samples but in the cold-worked metallurgical state. For the annealed samples T_m rises almost linearly with x from ~ 0 K for $x = 0.21$ to ~ 15 K for $x = 0.33$. In the same concentration range $\Delta\rho_m$ increases sharply from 0 to 0.07 $\mu\Omega$ cm. Such a value represents about 1.4% of the incremental resistivity $\rho(293\text{ K}) - \rho(4.2) \approx 5$ $\mu\Omega$ cm of the same 33-at.% Mn alloy.

It is to be noted that the result of high-temperature annealing is a striking increase of about 50% in both T_m and $\Delta\rho_m$ (Fig. 4). However, this is not accompanied by any significant change in the residual resistivity which means that the chemical order is essentially the same (on the scale of the electron mean free path) in the two metallurgical states. This is in some way consistent with neutron scattering measurements, which show that the development of short-range order in these alloys is very slow since even after an anneal of about an hour at 425°C there is no evidence for any short-range order.[8] Neverthe-

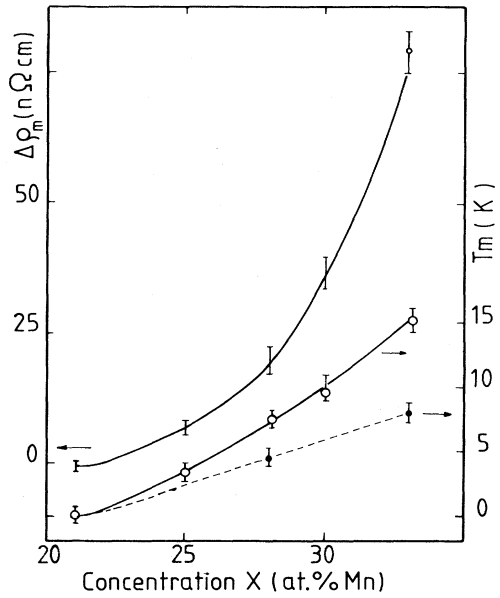

FIG. 3. Full curves represent the change with Mn concentration of the depth $\Delta\rho_m$ and the temperature T_m of the minimum in $\rho(T)$ of annealed $Ni_{1-x}Mn_x$ alloys. The dashed curve illustrates the concentration dependence of T_m in the same samples but in the cold-worked metallurgical state.

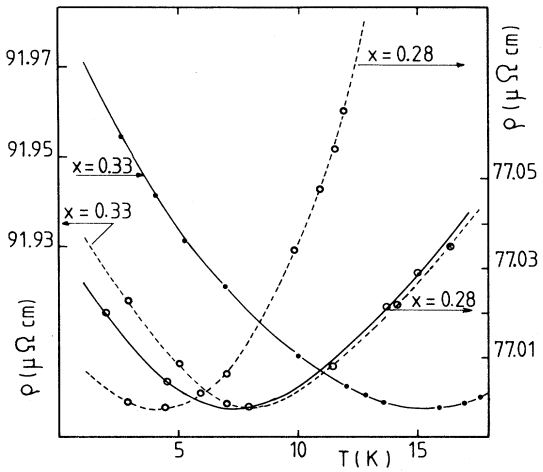

FIG. 4. Low-temperature-resistivity data on two samples, $Ni_{0.72}Mn_{0.28}$ and $Ni_{0.67}Mn_{0.33}$, differing by their metallurgical states. The full curves refer to the annealed state whereas the dashed curves correspond to the same samples but in the cold-worked metallurgical state.

less, the difference between the annealed (at 900°C) and cold-worked states might be due to very small changes in the local degree of magnetic order on an atomic scale or to the effects of dislocations on local alignment. Then, it is quite possible that such changes could have dramatic effects on the very small frustrated plaquettes and therefore on the properties of the mixed state.

According to the magnetic data $Ni_{1-x}Mn_x$ alloys are ferromagnetic for $x < 0.25$ and spin-glass-like above this composition. Now, from the variation with x of both $\Delta\rho_m$ and T_m (Fig. 3), we see that the anomalous behavior of $\rho(T)$ becomes vanishingly small as Mn concentration drops to about 21 at.%. It is thus clear that the resisitvity minima are mostly associated with either a pure spin-glass phase or a mixed phase in which the spin-glass character is probably the most dominant compared to the ferromagnetic one. From the arguments exposed in the introduction we believe in the existence of such a mixed state and ascribe the resistivity minima to the appearance of a transition from such a mixed state towards a ferromagnetic one. This claim is also corroborated by the fact that the variation of T_m and, more particularly, of $\Delta\rho_m$ with x (Fig. 3) bears resemblance to the transition line (T vs x separating the mixed and the ferromagnetic phases in Fig. 3 of Ref. 9). However, the transition reported here is rather gradual: It would start at very low T ($T \sim 0$ K) and continue up to some temperature which is naturally greater than T_m but which cannot be determined by resistivity measurements.[11]

In order to give added support to the above conclusion, we have carried out magnetoresistance measurements on the alloy $Ni_{0.72}Mn_{0.28}$. The results are given in Figs. 5 and 6 which we want to examine now.

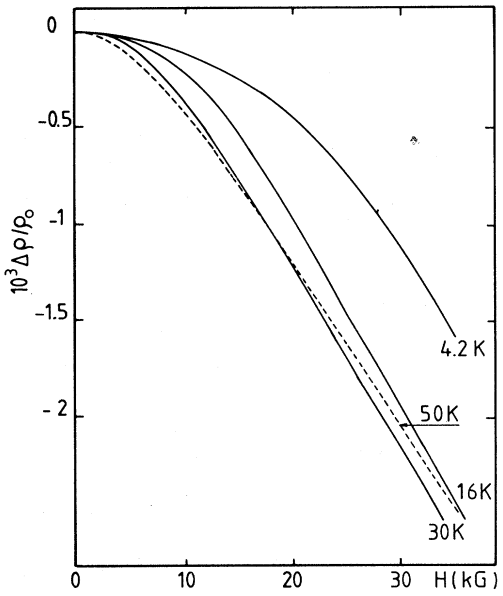

FIG. 5. Field dependence of the magnetoresistance of $Ni_{0.72}Mn_{0.28}$ at the indicated temperatures (zero-field cooled sample).

At the lowest temperature indicated in the figure ($T = 4.2$ K), $\Delta\rho/\rho_0$ varies approximately as H^2 over the whole range of the applied field (0–40 kG), that is,

$$\frac{\Delta\rho}{\rho_0} = \beta H^2 ,$$

with $\beta \sim 1.2 \times 10^{-6}$ (kG)$^{-2}$. Here ρ_0 is the residual resistivity at 4.2 K [$\rho_0 = \rho(4.2\text{ K})$ and

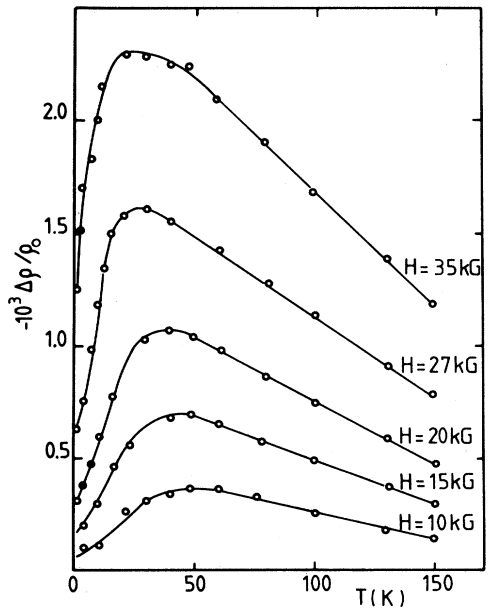

FIG. 6. Temperature dependence of the magnetoresistance of $Ni_{0.72}Mn_{0.28}$ in the indicated fields (zero-field cooled sample).

$\Delta\rho = \rho(T,H) - \rho_0]$. A quadratic behavior of this kind has been often observed in the magnetoresistance of the archetypical spin-glasses *Au*Fe and *Cu*Mn. Therefore the low-temperature behavior of $\Delta\rho/\rho_0$ of $Ni_{0.72}Mn_{0.28}$ seems to be suggestive of a spin-glass- (or related)like order. However, this behavior does not hold at higher temperatures: It is clear, from the figure, that the magnetoresistance in a given field increases with T and simultaneously evolves towards a linear variation as a function of H. This is particularly true for the 30-K curve which is governed by a linear behavior for $H \gtrsim 8$ kG. The variation of $-\Delta\rho/\rho_0$ with T for various fixed fields is given in Fig. 6. As can be seen there, $-\Delta\rho/\rho_0$ exhibits very defined maxima at a temperature in the vicinity of 30 K but which depends slightly on H. Now neither a maximum of this kind nor the emergence of a linear term of the form $-\alpha H$ are usual effects in archetypical spin-glasses. However, these two phenomena have been observed in *Au*Fe in the mixed-state concentration range ($\sim$ 15-at.% Fe) as well as in the quasiferromagnetic alloys *Pd*Fe and *Pd*Mn,[12] and are therefore suggestive of ferromagneticlike order.

We now briefly discuss some other possible scattering mechanisms which are predicted to lead to a singular behavior in the ρ versus T curve.

First of all, it seems quite natural to invoke the Kondo effect. Such a possibility can, however, be safely ruled out as we are considering strongly interacting magnetic systems [Curie and Néel temperatures of the pure substances are of the order of 627 K (Ni) and 85 K (Mn)] and the local magnetic moments associated with either Mn or Ni atoms are likely to be fully developed in these systems. Second, the resistivity minimum could be nonmagnetic in origin as it is thought to be the case in some amorphous alloys.[13] Then two distinct nonmagnetic effects could be envisaged.

A very interesting one is the localization phenomenon in highly disordered systems. At first sight this mechanism must be ruled out too since, according to the theoretical predictions,[14,15] the presence of very small amounts of magnetic impurities would cut off the resistivity singularity. The second one was proposed by Kondo[16] who showed that an impurity which could jump between two unoccupied atomic sites would give rise to a logarithmic decrease in $\rho(T)$. We shall comment further[11] on all the last alternative origins but here we emphasize that the three mechanisms just discussed have in common a logarithmic decrease of $\rho(T)$ which does not seem to be obeyed by our data (see inset of Fig. 2), even through the temperature interval (1.2–15 K) where the singular behavior is observed is too small to allow us to answer this point unambiguously at present.

Experimental evidence for a magnetic transition from a frustrated or mixed state towards a ferromagnetic state in zero applied field are reported. The results are in qualitative agreement with the theoretical predictions.[9] To the best of our knowledge it is the first time that a singular behavior in the resistivity of a highly frustrated magnetic alloy is observed at the lowest temperatures. A resistivity minimum has been observed in CoP ferromagnet in the amorphous state,[13] but in this case it could have a structural origin.

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