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Ferromagnetic Transitions in Ni-Mn Alloys

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Abstract

Ferromagnetic transitions in nickel and nickel-manganese alloys have been studied using resistivity-temperature measurements from 800 to 77 K. The results establish the transition temperature of nickel as 610 K and the transition temperature is shifted to lower values as the concentration of Mn in the alloy is increased. Analysis of the resistivity results near the ordering temperature ($T < T_c$) of these alloys suggest that these materials are in the same universal class as other ferromagnetic alloys.

Key Words: resistivity, transition temperature, spin disorder scattering, critical exponent

1. Introduction

Nickel has fcc structure at room temperature with a lattice constant of 3.52 Å. It has been reported [1] that it has an interatomic distance of 2.49 Å and atomic weight of 58.7. The ferromagnetic phase of this metal exists below about 630 K [2]. Manganese, on the other hand, has four allotropic forms namely α, β, γ and δ phases. The α-phase is stable below 700°C and it undergoes a paramagnetic-antiferromagnetic phase transition at about 95 K. The α-phase has a complex crystal structure [3] with 58 atoms in a body centered cubic structure of lattice constant 8.91 Å and with 29 atoms in a unit cell. These atoms are distributed over four crystallographically inequivalent sites [4]. The magnetic moments at sites I, II, III and IV are 1.9, 1.7, 0.6 and 0.2 μ_B, respectively, at 4.4 K. Neutron diffuse scattering study by Shull and Wilkinson [5] has indicated an average moment of 0.5 μ_B in the paramagnetic state up to 500 K. This is consistent with the four different moments with a weighted average of 0.63 μ_B obtained from neutron diffraction experiments by Yamada et al [6].

It has been reported [7-12] that the saturation magnetization of the disordered Ni-

Mn alloys increases linearly with increasing Mn content to about 6 at. % Mn, reaches a maximum at 10 at. % Mn, then decreases rapidly to zero near 25 at. % Mn. This behavior has been interpreted in terms of a nearest neighbor (NN) molecular-field model with ferromagnetic Ni-Ni and Ni-Mn and antiferromagnetic Mn-Mn interactions [9, 13, 14]. Long-wavelength neutron scattering experiments by Low et al [15,16] have found that the moment disturbance around Fe and Mn impurities in Ni is effectively confined to the solute atom site, differently from the case of Cr and V impurities. Moreover, polarized-neutron diffuse scattering experiments by Cable et al. [17,18] and NMR measurements on Ni-rich and Ni-Mn alloys by Kitaoka et al. [19] have shown that the magnetic state of Mn strongly depends on its NN environment. These results suggest that the magnetic moment of isolated Mn atoms is parallel to the magnetization of the Ni-matrix, whereas the Mn atoms with three or more Mn neighbor reduce or reverse its magnetic moment. The magnetic moments estimated by the NMR experiments by Kitaoka et al. [19] were found to be 3.0, 2.5 and -1.8 μ_B for isolated, reduced, and reverse moment Mn atoms, respectively. This existence of Mn atoms with reduced or reversed moments was shown by the calculation of the electronic structure of Ni-Mn alloys in the coherent potential approximation [20].

The electrical resistivity of Ni-Mn alloys containing up to 21.1 at. % Mn has been measured from 4.2 to 1000 K by Ikeda et al. [21]. With increasing Mn contents, the magnetic resistivity at $T \geq T_c$ in the disordered Ni-Mn alloys increases linearly, reaches a maximum around 7 at. % Mn and decreases. This behaviour is interpreted by the spin-disorder mechanism with consideration of the composition variations of not only the de Gennes factor but also the average exchange-interaction constant. Ikeda et al. [21] have taken the cusp of their resistivity-temperature curve as the transition temperature T_c. This is doubtful because it is in contradiction with magnetic scaling theory [22]. It is, however, suspected that the cusp (or the change in slope of $\rho - T$ curve) marks the onset of magnetic ordering.

In the present paper, we report on the ferromagnetic transitions in Ni and Ni-Mn alloys, the alloys containing up to 30 at. % Mn. A significant contribution is being made here in the determination of T_c and the effect of Mn concentration on the transition temperature of these alloys. Bearing in mind the high Curie temperature of the host metal and the Néel point of α-Mn which has been established as 90 $\pm$ 1 K [23], it is very unlikely for the Curie temperatures of these alloys (even that with the highest concentration of Mn) to be located below 90 K. It was therefore not found expedient to work below 77 K.

2. Experimental details

The starting materials were 99.98 % Ni, 5 at. % Mn in Ni, 10 at. % Mn in Ni, 15 at. % Mn in Ni, 20 at. % Mn in Ni, 25 at. % Mn in Ni, and 30 at. % Mn in Ni, all obtained from BDH Chemicals Ltd. The specimens were first cleaned with dilute solution of HCl in methanol to remove surface oxides and other contaminants. They were then dried and cut into thin rectangular forms 2.0cm $\times$ 0.40cm $\times$ 0.20cm. Potential probes to these

specimens were separated by 1.6cm, whilst current probes were made at the ends of the longest dimension.

Resistance measurements were made by using a constant current source and a potentiometer. The measuring current was drawn from an electronically controlled constant current supply, which was variable in steps from about 1.0 to 16 mA.. The precise value of the current could be measured since it flowed through a standard 10-Ω resistor in series with the specimen and the potential difference across this could be measured on the same potentiometer as was used for measuring the potential difference across the specimens. The main potentiometer for the measurement of the potential difference between the voltage probes was a Tinsely precision vernier potentiometer. A Tinsely photocell amplifier was used in conjunction with the potentiometer and this could provide much more amplification than was necessary. The temperature of the 99.98 % Ni, 5 at. % Mn in Ni and 10 at. % Mn in Ni specimens was varied by using an electrothermal Bunsen capable of producing a maximum power of 1.5 kW. These temperatures were monitored with a copper - alumel thermocouple. Specifically for the 15 at. % Mn in Ni up to 30 at. % Mn in Ni specimens, a conventional N_2 cryostat with a temperature control unit in the working range of 77 to 600 K was used. Temperatures in this range were measured with a copper resistance thermometer incorporated with the cryostat. Resistance measurements were made as described for the three previous specimens.

3. Results and Discussion

3.1 Electrical resistivity and the Curie temperature of Ni and Ni-Mn alloys.

Figure 1 illustrates the temperature derivative of the resistivity versus temperature of the Ni specimen with an overlay of its resistivity versus temperature curve. The resistivity first falls slowly from 32 $\mu\Omega$ cm at 800 K to 28 $\mu\Omega$ cm at 670 K. It then drops sharply to 14 $\mu\Omega$ cm at 540 K and finally falls gently to 7 $\mu\Omega$ cm at 300 K.

Zumteg and Parks [24] have defined the transition temperature as that temperature at which the temperature dependent magnetic coherence length ξ, approximately equals the phonon limited mean free path of the conduction electrons. Craig and Goldburg [22] have suggested that the anomaly in the temperature derivative of the resistivity that gives a singularity marks the transition from the hydrodynamic regime to the critical regime predicted by the magnetic scaling theory, and the anomaly is believed to lie in the strong temperature dependence of the phonon-limited mean free path in the neighbourhood of the ordering temperature. This hydrodynamical - critical transition is defined by the position of the singularity in the temperature derivative of the resistivity versus temperature curve. Consequently a plot of $\delta\rho/\delta T$ against temperature defines the Néel point T_N in antiferromagnets and the Curie point T_C in ferromagnetics. The transition displayed in Fig. 1 establishes T_C in nickel as 610 K. The slope $\delta\rho/\delta T$ was calculated by drawing a straight line through three adjacent points of the $\rho - T$ curve and the gradient taken for the average temperature of the three points.

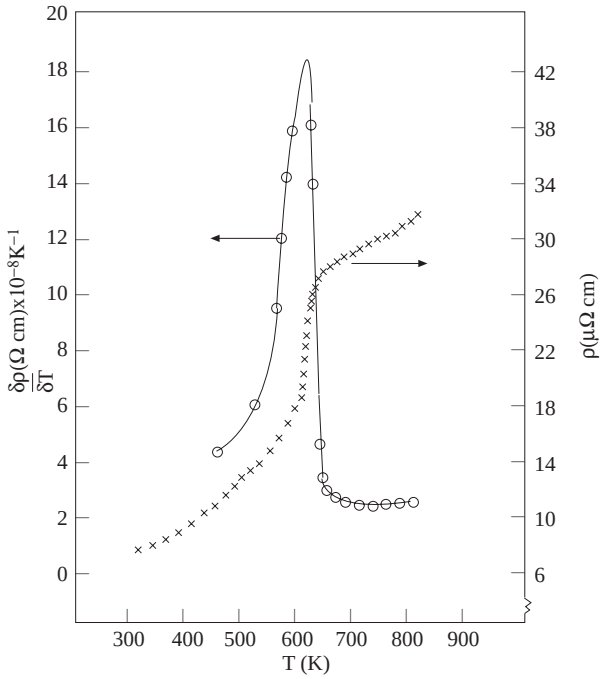


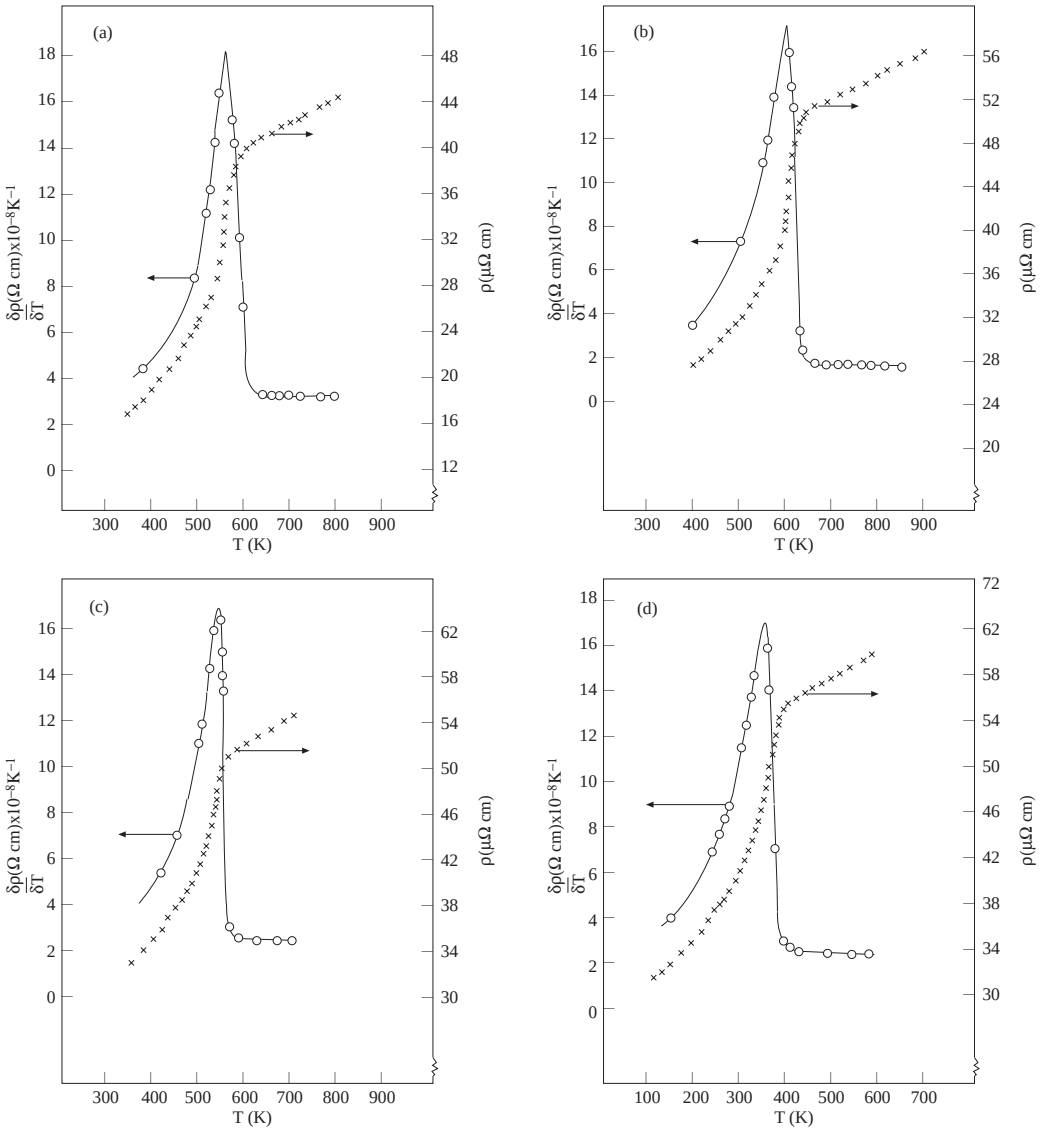
Figure 1. $\delta\rho/\delta T$ versus T curve of 99.98 % rich Ni with an overlay of its ρ versus T curve.

Figures 2 (a, b, c, d, e, f) illustrate the temperature derivative of the resistivity versus temperature of the 5 at. % Mn in Ni, 10 at. % Mn in Ni, 15 at. % Mn in Ni, 20 at. % Mn in Ni, 25 at. % Mn in Ni and 30 at. % Mn in Ni specimens, respectively. The curves are drawn with their corresponding overlay of resistivity versus temperature curves. Placing these results in the context of the results of Ikeda et al. [21], it is observed that our transition temperatures are lower. Figure 3 illustrates a plot of the Curie temperature of the Ni-Mn alloys as a function of Mn concentration. Mn-concentration dependence of the Curie temperature, which had been determined by Wise [25] using magnetization measurements and the results of Ikeda et al. [21], is presented on the same scale. It can be observed from the plots that for a given concentration of Mn, The Curie temperature is lower for our alloys in this coverage, suggesting that the change in slope of the $\rho - T$ curve of the previous workers [21] marks the onset of magnetic ordering.

The high resistivities of the transition metals has been explained by a model proposed by Kasuya [26]. He attributes the high resistivities of these metals to be due to spin disorder scattering. Furthermore, the model is able to explain the abrupt fall in resistivity near the ordering temperature.

On alloying Ni with Mn, it is likely that the exchange energy of the matrix atoms is reduced. This reduction may be caused by the departure from the normal Ni lattice as the Mn atoms are introduced into the Ni. Since the spins of the Ni atoms are no longer at

their normal ordered state upon the introduction of Mn, it may require less thermal energy to overcome the exchange forces coupling the spins of the matrix alloys as compared to the situation of pure Ni. T_c may therefore be reduced and as the concentration of the Mn increases the degree of disorder of the spins is likely to increase and T_c is further reduced. The complex crystallographic structure of α-Mn and its average moment of 0.5 μ_B in the paramagnetic state are therefore likely to play a role in establishing the Curie temperatures of these alloys.



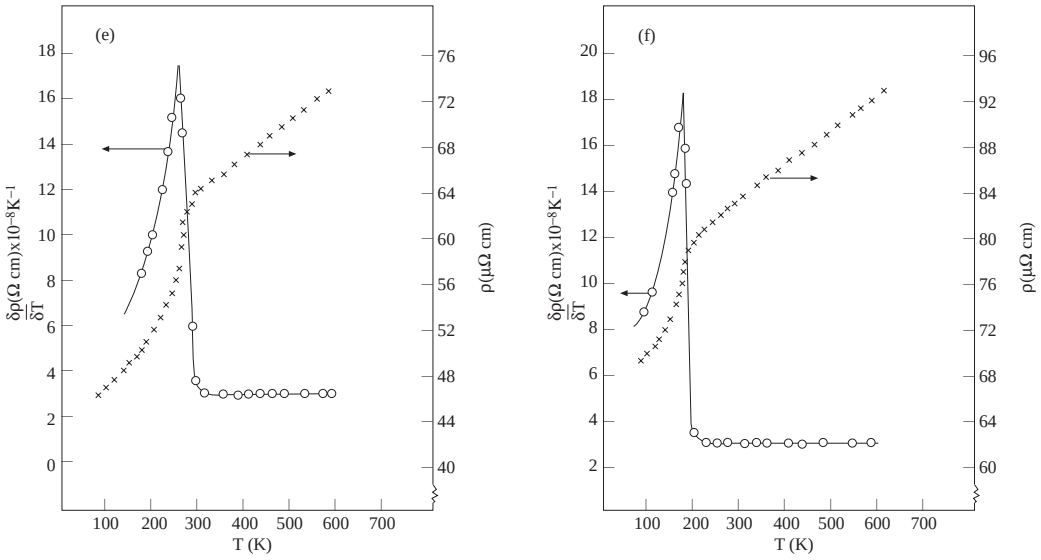


Figure 2. $\delta\rho/\delta T$ versus T curves of Mn in Ni specimens with overlay of the ρ versus T curves: (a) 5 at. % of Mn, (b) 10 at. % Mn, (c) 15 at. % Mn, (d) 20 at. % Mn, (e) 25 at. % Mn, and (f) 30 at. % Mn.

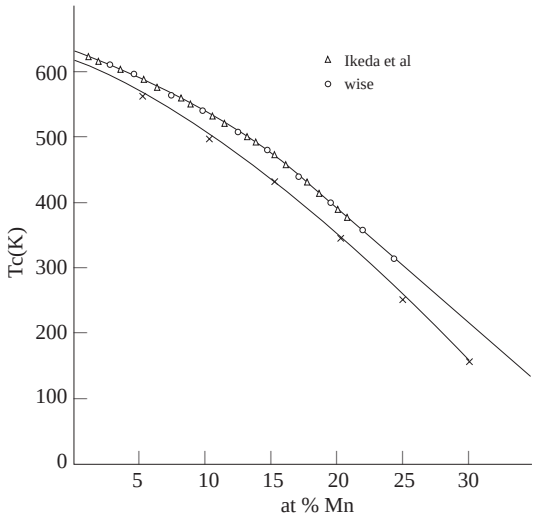


Figure 3. Mn-concentration dependence of the Curie temperature

3.2. Critical exponents of Ni-Mn alloys

One effect of magnetic ordering on the scattering of conduction electrons in ferromagnetic alloys is to introduce anomalies in the electrical resistivity near the ordering temperature. de Gennes and Friedel [27] have explained the effect of spin fluctuations in localized moment ferromagnets within a mean field approximation and found the anomaly in the temperature derivative of the electrical resistivity to vary as $\ln|(T-T_c)/T_c|$. Alexander et al. [28] have concluded that in ferromagnetic metals as far as their critical exponents are concerned they obey a relation of the form

$$\partial\rho/\partial T = A \in^{-\lambda} \propto C_p \text{ at } T < T_c, \tag{1}$$

where $\in = |(T - T_c/T_c|$. Therefore $\ln \partial\rho/\partial T = A_t - \lambda \ln|(T - T_c/T_c|$, and a plot of $\ln \partial\rho/\partial T$ versus $\ln|(T-T_c)/T_c|$ gives directly the exponent λ which is the slope.

These plots for specimens $Ni_{100-x}Mn_x (x = 0, 5, 10, 15, 20, 25, 30)$ are presented in Figure 4. The results shown in Table 1 give the critical exponent for 99.98% Ni as 0.08, consistent with Fisher [29] and Heller [30], who have determined the exponent to be of the order of 0.1 or less. In the case of the alloys, the exponents are substantially high. It is interesting to note that the exponent rises from 0.34 for 5 at. % Mn to a maximum of 0.52 for 10 at. % Mn and then decreases to 0.27 for 30 at. % Mn. These results may be interpreted in a similar way in terms of the nearest neighbour (NN) molecular field model with ferromagnetic Ni-Ni and Ni-Mn and antiferromagnetic Mn-Mn interactions [9,13,14]. Mn is regarded as a key material lying on the border between the phenomena of itinerant ferromagnetism with spin fluctuations playing an extremely important role in its properties. Critical exponents of 0.65 for $T < T_N$ and 0.40 for $T > T_N$ have been determined [31] using resistivity-temperature measurements. To this end, the alloys studied in this work may therefore be classified as other universal ferromagnetic alloys.

Table 1. Critical exponents of Ni-Mn alloys

Sample	Curie temperature T_c (K)	Critical exponent, λ
99.98% pure Ni	610	0.08
5 at. % Mn	550	0.34
10 at. % Mn	500	0.52
15 at. % Mn	440	0.43
20 at. % Mn	350	0.38
25 at. % Mn	250	0.35
30 at. % Mn	180	0.27

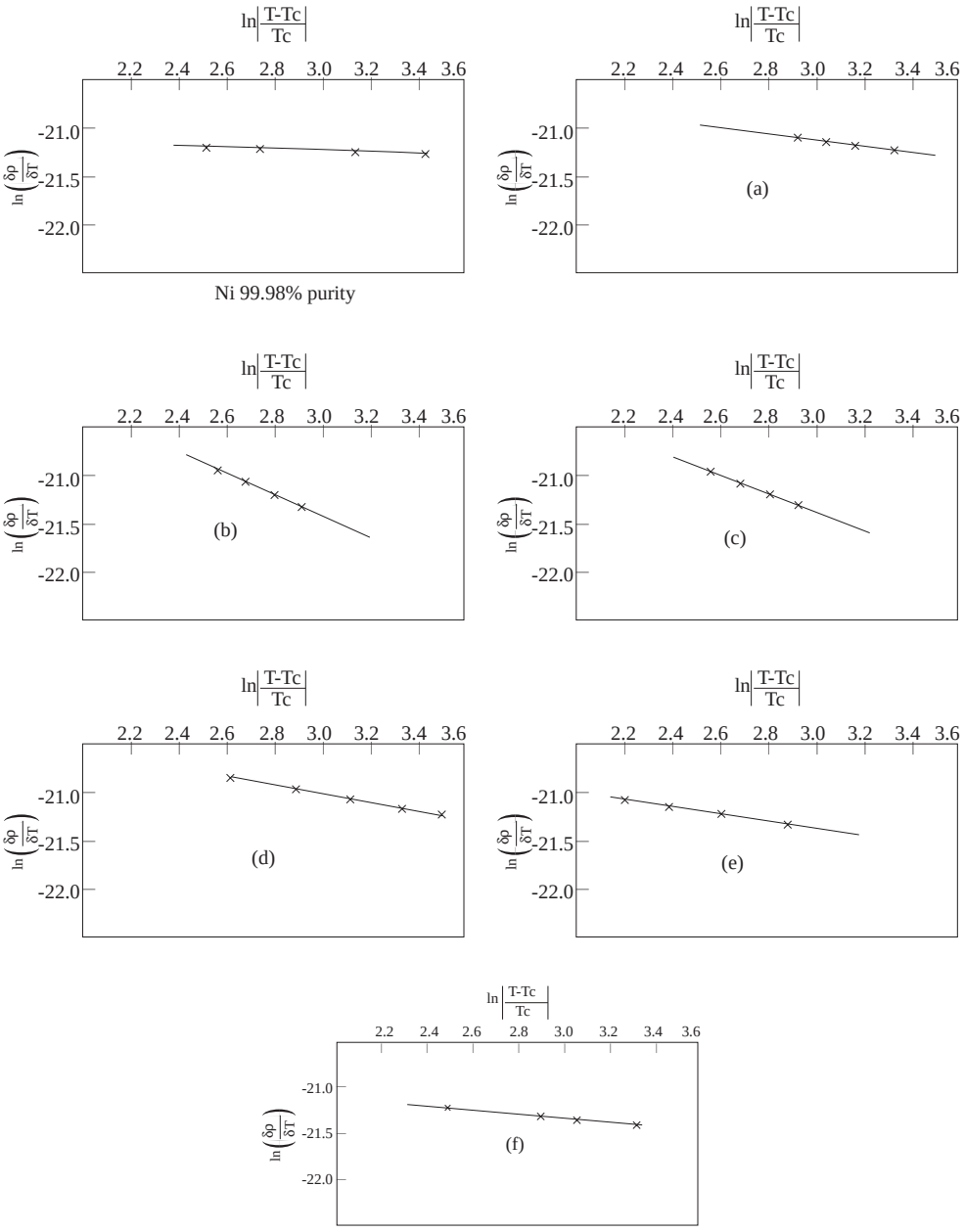


Figure 4. ln $(\partial\rho/\partial T)$ versus $|(T - T_c)/T_c|$ of 99.98 % Ni.
(a) 5 at. % Mn, (b) 10 at. % Mn, (c) 15 at. % Mn, (d) 20 at. % Mn,
(e) 25 at. % Mn, (f) 30 at. % Mn

4. Conclusion

The results establish the transition temperature of Ni as 610 K. The transition temperture is shifted to lower values as the concentration of Mn in the alloy is increased. The transition temperatures of these specimens are lower than those reported by other workers. It is therefore likely that the transition temperatures determined by previous workers mark the onset of paramagnetic-ferromagnetic transitions. The analysis of the resistivity results near the ordering temperature ($T < T_c$) of these alloys suggest that these materials are in the same universal class as other ferromagnetic alloys.

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