THE ANOMALOUS LOW TEMPERATURE RESISTIVITY AND
CRITICAL SCATTERING OF CONDUCTION ELECTRONS
AROUND THE NÉEL POINT OF $\alpha$-Mn FILMS CONTAINING
DILUTE CONCENTRATION OF Ni

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Abstract—Electrical resistivity measurements on thermally evaporated Mn$_{100-x}$Ni$_x$ films (with $x = 0.01, 0.02$
and 0.05 at.% Ni) have been performed over the temperature range from 300 to 1.4 K using the van der
Pauw four probe technique. The Néel point ($T_N$) of the films determined using the model of Graig and
Goldburg reveals a shift to upper values as the concentration of Ni is increased. Analysis of the resistivity
data near the Néel points of these alloys gave critical exponents which are in moderate agreement with
existing theories. The low temperature resistivity of the 0.02 and 0.05 at.% Ni in Mn specimens obeys a
$T^2$ law indicating a spin fluctuation scattering mechanism in these alloys.

Keywords: Resistivity; Critical exponent analysis; Antiferromagnetic transition

1. INTRODUCTION

$\alpha$-Mn has a cubic structure with a lattice constant of
8.91 Å and contains 58 atoms per unit cell. It has been
shown by Bradley and Thewlis [1] that the structure
contains four crystallographically nonequivalent sites
referred to as sites I, II, III and IV. The basis of the
whole arrangement is a simple body-centred cubic lat-
tice with each lattice point being associated with a
cluster of 29 atoms. Around each site-I atom is an
octahedron of site IV atoms, the opposite faces of the
octahedron being of different sizes so that the sym-
metry is tetrahedral. The four site-II atoms are some-
what further from the centre of the group and are
arranged tetrahedrally about the centre. The 12 outer-
most site-III atoms comprise a polyhedron having
cubic and octahedral faces. The whole cluster has
symmetry, which is tetrahedral, as is that of the crys-
tal as a whole.

$\alpha$-Mn in many respects is analogous to an inter-
metallic compound. Indeed, an intermediate phase
generally called the $\chi$ phase, has a structure iso-
morphous with $\alpha$-Mn. This $\chi$ phase has been ident-
ified in several binary [2–5] and ternary alloys. Two

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factors should appear to be in operation in stabilising
both $\alpha$-Mn and the $\chi$ phase. These are their electronic
structure and atomic sizes.

The coordination numbers (CN) of sites I, II, III
and IV are, respectively, 16, 16, 13 and 12 [3]. There
is a striking difference between inter-atomic distances
within the Mn structure, as well as coordination num-
bers associated with the various sites. The inter-
atomic distances vary from 2.21 to 2.96 Å [3] and
the coordination numbers vary from the compact icos-
ahedral with coordination number 12, to sites with
coordination number 16 which occupy considerably
more volume. From consideration of space filling, it
would appear that the Mn atoms in sites I and II
would tend to have larger electronic radii in order to
fill the relatively larger volume of the coordination
number 16. Smaller atoms, on the other hand, would
occupy the sites III and IV, since there is smaller vol-
ume associated with the coordination numbers of 13 and 12.

A number of neutron diffraction studies [6–9] have
shown that antiferromagnetism occurs below 95 K
($T_N$) and that the magnetic moments differ at the four
different sites. Several authors [10–12] have tried to
explain the magnetism of $\alpha$-Mn by static spin density
waves. On the other hand, neutron diffraction experi-
m ents on single crystal $\alpha$-Mn by Yamada et al. [9]
have shown that the magnetic structure can be
described by a localised-moment model, rather than a
spin density wave model with a simple non-collinear configuration, and that the moments at sites I, II, III and IV are 1.9, 1.7, 0.6 and 0.2 $\mu_B$, respectively, at 4.4 K.

From consideration of atom sizes, predictions can be made with regards to the effect of alloying. One may expect atoms of relatively smaller sizes, such as Fe and Cr, to preferentially occupy the smaller sites III and IV. Studies of Fe dissolved into $\alpha$-Mn have shown this to be the case [3, 4]. On the other hand, relatively larger atoms, such as Mo, Re and Ru, might be expected to preferentially occupy the larger sites I and II. This has been shown to be true for Mo in the $\chi$-phase alloy $\text{Mo}_1\text{Cr}_2\text{Fe}_{62}$ [4, 5] where the Mo atoms were found to preferentially occupy the I and II sites, leaving the smaller sites to Fe and Cr.

The Mn–Ni alloy system is very complicated and may not be easy to investigate since its properties depend on the details of the microstructure, the distribution of Ni atoms in the alloy and consequently the way and how far Mn atoms interact with each other. Depending on the subtle changes in its chemical and topological environment, Mn may exhibit largely different spin states and exchange interaction with its neighbours. The result is that such alloys present a wealth of magnetic states, ferromagnetic and antiferromagnetic spin glass properties. In this communication we report on the resistivity–temperature curves of thermally evaporated Mn$_{100-x}$Ni$_x$ thin films and their respective Néel points using a model proposed by Craig and Goldburg [13].

2. EXPERIMENTAL DETAILS

The starting materials were 0.01, 0.02 and 0.05 at.% Ni in Mn all obtained from BDH Chemicals Ltd, Poole, England. The purity of each component of the Mn–Ni alloy is quoted by the manufacturers as 99.9998%. The films were prepared by thermal evaporation on to thin glass substrates cut to size and cleaned. Each alloy was first cleaned in 5% HCl in methanol to remove surface oxides and other contaminants. They were then dried and ground immediately before being loaded into a previously cleaned molybdenum boat. The melting points of Mn and Ni are 1260 and 1455°C, respectively [14]. Since the components may evaporate at different rates because of their different vapour pressure, a flash evaporation (with a rate ∼300 Ås$^{-1}$) was used for all the films from the original component. An AUTO 306 coating unit from Edwards High Vacuum Ltd was used in this operation. This unit has a radiant heater capable of maintaining substrate temperatures up to 350°C. The substrates were thin glass slides, which were cut into squares of side 8 mm to fit into an $\alpha$-brass mask designed to produce the required film shape. The glass pieces which were to serve as substrates were cleaned in Genklene before being placed...
in position in the mask. In these experiments the substrates were held at 300°C for each deposition. Substrate temperatures were measured with a copper constantan thermocouple incorporated with the unit. To achieve the correct substrate temperature the hot junction of the thermocouple was screwed on to the mask. Film thicknesses were measured with an interferometer and the ambient pressure in the bell jar was measured with an ion gauge incorporated into the unit. The ambient pressure was kept at 2×10⁻¹⁰ Torr for each specimen. To achieve this the unit was pumped done for 8 h for all the specimens under investigation. Resistivity measurements between 300 and 1.4 K were carried out by the van der Pauw four probe method in a conventional He⁴ cryostat as described by Swallow [15]. Temperatures between 300 and 60 K were measured with a copper resistance thermometer. Below 60 K, the copper resistance thermometer was insensitive and an Allen–Bradley carbon resistor was used. This has a resistance of about 200 Ω at 25 K and rises to about 300 Ω at 4.2 K. This sensor is therefore extremely sensitive for temperatures below 4.2 K. In conjunction with this sensor, temperatures below 4.2 K were measured with a gas thermometer. These temperatures were deduced directly from He⁴ vapour pressure with an accuracy of about 0.5%. Above about 2 K the vapour pressure was measured with mercury manometer and below 2 K it was measured with an oil manometer filled with low vapour pressure Apiezon 704 oil. The oil manometer was calibrated against the mercury manometer around about 2 K. Calibration checks were also made around these temperatures with the Allen–Bradley carbon resistor.

3. RESULTS AND DISCUSSION

3.1. Electrical resistivity and the Néel point of Mn–Ni films

Figures 1–3, respectively, illustrate the derivative of the electrical resistivity with respect to temperature δρ/δT, versus temperature of the 0.01, 0.02 and 0.05 at.% Ni in Mn specimens with overlays of their corresponding resistivity–temperature curves. Referring to Fig. 1, the resistivity–temperature curve of the 0.01 at.% Ni in Mn film is similar to that of pure α-Mn film studied by Boakye et al. [16–18]. There is firstly a gradual drop in resistivity as the temperature is lowered from 300 K. This behaviour is attributed to the phonon scattering of the conduction electrons. The resistivity goes through a minimum at a temperature of 118 K before rising to a maximum. At temperatures below the maximum point, which corresponds to T ≈ 75 K, the resistivity falls very sharply. This rapid decrease in resistivity due to the magnetic ordering of the spins does not, however, give the residual resistivity ρ₀ to be zero as would be expected in a pure and perfect specimen of a magnetic metal but rather tends to a relatively high value of 0.93 μΩ m as compared with 0.81 μΩ m of the α-Mn film results of Boakye et al. [16–18]. This increase in the residual resistivity from 0.81 for α-Mn to 0.93 μΩ m is what one might expect from Matthiessen’s rule.

Referring to Figs 2 and 3, the temperatures corresponding to the resistivity minimum, Tₘₐₓ₁ of the 0.02 and 0.05 at.% Ni in Mn films are 120 and 125 K, respectively. The resistivity maxima are observed, respectively, at 75 and 80 K. The different features exhibited in Figs 2 and 3 are the occurrence of low temperature resistivity minima which appear at 10 and 15 K, respectively. Nagasawa and Sembu [19] have suggested an explanation from their data on alloys of manganese with transition metal impurities. Their results reveal a low temperature resistivity
minimum in the neighbourhood of 15 K and below $T_{\text{min}}$ corresponding to the temperature of the resistivity minimum, the resistivity obeyed a $T^2$ law. They therefore suggested that the presence of transition metal impurities in $\alpha$-Mn gives rise to a distortion of the magnetic moments of the surrounding manganese atoms, thus leading to spin fluctuation scattering on the conduction electrons. A similar distortion of the magnetic moments has been reported in the Ni–Rh alloy system [20]. There appears to be some similarity with the results of two of our specimens, namely 0.02 and 0.05 at.\% Ni in Mn and those of Nagasawa and Semba [19]. Plots of the resistivity against $T^2$ of the 0.02 and 0.05 at.\% Ni in Mn below $T_{\text{min}}$ are illustrated in Fig. 4. These plots revealing a $T^2$ law below $T_{\text{min}}$ are also in agreement with the spin fluctuation
theory given by Murayama and Nagassawa [12]. Accordingly, the low temperature resistivity minimum shown by our two samples (0.02 and 0.05 at.% Ni in Mn) may be explained in terms of spin fluctuations. The present results reveal a residual resistivity $\rho_0$ of 1.08 and 1.16 $\mu\Omega$ m for the 0.02 and 0.05 at.% Ni in Mn, respectively. A plot of the residual resistivity $\rho_0$ versus Ni concentration is illustrated in Fig. 5. This plot reveals an increase in residual resistivity with increasing Ni concentration as one might expect from Matthiessen’s rule but does not appear to follow a definite relationship, presumably due to the inadequate data (with only three points).

Zunteg and Parks [21] have defined the Néel point as that temperature at which the temperature-dependent magnetic coherence length $\xi(T)$ approximately equals the phonon limited mean free path of the conduction electrons. Craig and Goldburg [13] have sug-
suggested that the anomaly in the derivative of the resistivity with respect to temperature that gives singularity marks the transition from the hydrodynamic regime to the critical regime predicted by the magnetic scaling theory and the anomaly lies in the strong temperature dependence of the phonon limited mean free path in the vicinity of the ordering temperature. This hydrodynamical critical transition is defined by the position of the singularity in the $\delta \rho / \delta T$ versus temperature curve. Consequently, using the resistivity temperature data a plot of $\delta \rho / \delta T$ versus temperature gives a spike which defines the Néel point. The temperature derivative 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. The Néel points of the alloys, using this model, have been established as can be seen in Figs 1–3 as 90±1, 95±1 and 100±1 K for the 0.01, 0.02 and 0.05 at.% Ni in Mn, respectively, suggesting a shift of $T_N$ to upper values as the concentration of Ni is increased.

3.2. Critical exponents of Mn–Ni films

One effect of magnetic ordering on the scattering of conduction electrons in magnetic metals is to introduce anomalies in the electrical resistivity near the ordering temperature. Suezaki and Mori [22] have studied the anomaly as follows:

$$\delta \rho / \delta T = -B_0 K e^{-(\alpha + \gamma)^{-1}},$$

for $T > T_N$

where the constant $B_0$ incorporates terms involving the zone boundary energy gap $B_g$.

$$\delta \rho / \delta T = -B_0 e^{-(\alpha + \gamma)^{1/2}} + B_0 e^{-(\alpha + \gamma)^{1/3}}$$

for $T < T_N$, where $\epsilon = (T-T_0)/T_N$

The term involving $B_0$ will be dominant at temperatures less than $T_N$ because the scaling factor law gives $(\alpha + \gamma)/2 - (\alpha + \gamma - 1) = \beta$ which is positive, and if $T$ approaches $T_N$ the first term is negatively divergent and becomes more important. Localised spins treated with the isotropic Heisenberg model with a large spin give $\alpha = 0$ and $\gamma = 4/3$. From the above expressions,

$$\delta \rho / \delta T = -B_0 e^{-2\beta^{1/3}} + B_0 e^{-1/3},$$

for $T < T_N$

and

$$\delta \rho / \delta T \approx e^{-1/3},$$

for $T > T_N$.

Alexander et al. [23] have concluded that in antiferromagnetic materials as far as values of the critical exponent $\lambda$ are concerned, they are to obey the relationship of the form $\delta \rho / \delta T \propto e^{-\lambda}$. Figures 6(a–c) illustrate plots of $\ln(\delta \rho / \delta T)$ versus $\ln(T-T_N)/T_N$ of the same specimens for $T > T_N$. The above theory [22] shows that when $T < T_N$, $\delta \rho / \delta T = B_0 e^{-(\alpha + \gamma)^{-1}}$. This can be expressed in a more usable form as

$$\ln(\delta \rho / \delta T) = \ln B_0 - \lambda \ln(T-T_0)/T_N.$$

The slopes of Figs 6(a–c) and 7(a–c) give $\lambda$ for $T < T_N$ and $T > T_N$, respectively. A summary of the present results together with those of Boakye et al. [16–18] is given in Table 1. It can be seen from these results that there is not quite a significant change in the critical exponents. This might be presumably due to the dilute concentration of the Ni.

4. CONCLUSION

The present results reveal that the Néel points of Mn–Ni alloys shift to upper values with increasing concentration of Ni. Analysis of the resistivity–temperature results near the Néel points gave critical exponents, which are in moderate agreement with existing theories. The low temperature resistivity of the 0.02 and 0.05 at.% Ni in Mn samples obeys a $T^2$ law indicating a spin fluctuation scattering mechanism in these specimens.

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