

Antiferromagnetic Transition in Thermally Evaporated Manganese-Vanadium Alloys

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Abstract

Antiferromagnetic transition in thermally evaporated Mn-V alloys has been studied using resistivity-temperature measurements from 300 to 1.4 K. Resistivity-temperature behaviour typical of bulk α -Mn rich specimen is obtained with 0.05 at % V in Mn. The Néel point is shifted to 86 ± 1 K from the value of 90 ± 1 K known for pure α -Mn. The Néel point is shifted further to lower values as the concentration of V in Mn increases. Below the temperature corresponding to the low temperature resistivity minimum, the resistivity obeys a T^2 law, suggesting that vanadium impurities in the manganese film gives rise to a distortion of the magnetic moment of the manganese atoms and thus leading to spin fluctuation scattering on the conduction electrons.

Key Words: Néel point, magnetic moment, spin fluctuation.

1. Introduction

Manganese is one of the strangest of metallic conducting elements. It has a body-centred cubic structure with 58 atoms in a unit cell made up of two clusters of 29 atoms each. The 29 atoms in each cluster are distributed over four crystallographically inequivalent sites: one atom at site I with 16 nearest neighbours, four atoms at site II with 16 nearest neighbours each, 12 atoms at site III with 13 nearest neighbours each and 12 atoms at site IV with 12 nearest neighbours each. The cube edge is of length 8.91 \AA [1]. α -Mn is only one of four allotropic forms in which manganese metal crystallises, the others are the β , γ and δ phase. The α -phase is stable below $700 \text{ }^\circ\text{C}$.

Atoms at the various sites in α -Mn have been shown to have localised magnetic moments from neutron diffraction experiments. The magnetic moments associated with site I, II, III and IV are 1.9, 1.7, 0.6 and $0.25\mu_B$, respectively, below the Néel point [2]. These values have been confirmed by Yamagata and Asayama [3] using NMR techniques at helium temperatures. These values indicate that the magnetic moment at any particular site is critically dependent upon the atomic environment and the size of the atom cage surrounding the manganese atom. One interesting characteristic of α -Mn is its transport properties. The resistivity of α -Mn depends on T^2 at temperatures below 20 K [4-6]. This has been confirmed by Boakye and Grassie [7] in their experiments using thin films of evaporated Mn. The coefficient of T^2 is anomalously large, being the largest coefficient known for pure metals. Nagasawa and Semba [8] have measured the resistivity of α -Mn alloys containing dilute V, Cr, Fe, Co and Ni impurities and observed a drastic change in the coefficient of T^2 upon addition of transition-metal impurities.

Specifically, a change in the sign of the coefficient and resistance-minimum phenomenon were observed for the alloys containing V, Co and Ni impurities. These results are considered to be analogous to the Kondo effect, implying the existence of fluctuations of impurity spins in antiferromagnetic α -Mn. It is therefore being suggested that the rapid spin fluctuations of α -Mn in the paramagnetic state have a strong effect, even below the Néel point, on such physical properties as the anomalously large T^2 term coefficient for the resistivity, and on the small magnetic moments of the Mn atoms at sites III and IV.

It has been shown [5, 9] that pure α -Mn exhibits a sharp cusp in the resistivity-temperature curve around 95 K. This temperature corresponds to the temperature at which antiferromagnetism sets in. Thus this minimum has been thought to be associated with the ordering temperature T_N . Coles [10] has suggested that such changes in the resistivity-temperature curve can be explained by the presence of a large spin-disorder resistivity above the Néel temperature. The temperature dependence of this resistivity anomaly depends on the amount and type of impurities in the sample.

This paper reports on the resistivity-temperature curves of thermally evaporated $\text{Mn}_{100-x}\text{V}_x$ thin films (with $x = 0.05, 0.5,$ and 1 at % V) and their respective Néel points using a model proposed by Craig and Goldburg [11]. The resistivity anomalies at low temperatures ($T < 10$) giving rise to spin fluctuations are also investigated.

2. Experimental Details

The starting materials were 0.05 at % V in Mn, 0.5 at % V in Mn and 1 at % V in Mn, all in the form of flakes obtained from Aldrich of Milwaukee, Wisconsin, USA. The purity of each component of the Mn-V alloy, quoted by the manufacturer, is 99.998%. The flakes were first cleaned in 5% HCl in methanol to remove surface oxides and ground to coarse powder before loaded into a cleaned molybdenum boat. An AUTO 306 coating plant from Edwards High Vacuum Ltd., Sussex, UK was used in this operation. This coating unit has a radiant heater capable of maintaining substrate temperatures up to 350 °C. In these experiments glass substrates previously cleaned were held in a brass mask. The substrates were held at 150 °C for each evaporation, a flash deposition rate on the order of 300 Ås⁻¹ was used for each specimen. The deposition rates were monitored with a quartz crystal thickness monitor. Substrate temperatures were measured with a copper-constantan thermocouple incorporated with the unit. The ambient pressure in the bell jar was measured with an ion gauge. The actual thicknesses of the films were measured with a Varian interferometer. The ambient pressure was kept at 2×10^{-6} T for all samples. To achieve this, the unit was left pumping for about 8 h. The cryostat used in these experiments was of a conventional design as described by Swallow [12]. Resistivity measurements were made by the van der Pauw four-probe technique [13]. Temperatures between 300 and 60 K were measured with a copper resistance thermometer. Below 60 K, copper resistance thermometer is insensitive and carbon resistance thermometer was used.

Temperatures below 4.2 K were obtained by condensing liquid helium into the insert of the cryostat and pumping on it. In conjunction with the carbon resistance thermometer, temperatures below 4.2 K in the specimen chamber of the cryostat were measured with a gas thermometer.

3. Results and Discussion

3.1. Electrical resistivity of MnV thin films

In Figure 1 are plotted the electrical resistivity-temperature curves, with each vanadium concentration identified by the labels MnV1, MnV2 and MnV3. Curve MnV1 is similar to the resistivity temperature curves reported on Mn-rich films by Boakye et al [7]. Firstly there is a gradual linear drop in resistivity as the temperature is lowered from 300 K. The behaviour is attributed to the phonon – scattering of the conduction electrons. The gradient from this portion of the curve is $2.80 \times 10^{-4} \mu\Omega\text{K}^{-1}$. This value is lower

than the value deduced from the curve for pure Mn-rich film reported by Boakye et al [7]. The resistivity goes through a minimum at a temperature of 95 K before rising to maximum at a temperature of 70 K. At temperatures below the maximum point the resistivity falls very rapidly. This sharp decrease in the resistivity, due to the magnetic ordering of the spins, does not give the residual resistivity to be equal to zero, as would be expected in a pure and perfect specimen of magnetic metal, but rather tends to a high value of resistivity ($0.90 \mu\Omega\text{m}$) compared to $0.80 \mu\Omega\text{m}$ reported on α -Mn rich film by Boakye et al [7] and $0.07 \mu\Omega\text{m}$ reported by Meaden and Pelloux-Gervais [9]. The increase in residual resistivity is what one might expect from Matthiessen's rule. The resistivity temperature curves MnV2 and MnV3 are also illustrated in Figure 1. The different features shown by these curves is the occurrence of a low temperature resistivity minimum which appears at 10 K in MnV2 and 12 K in MnV3, respectively. A number of possible explanations have been considered in an effort to explain the occurrence of the low temperature anomalies in these two samples. Firstly there is a possibility of yet another phase change occurring in the low temperature region where the minimum occurs. One could then postulate a reduction in the number of current carries, or a modification of their properties, that could lead to an increase in resistivity, just as the temperature is decreased below the transition temperature. Nagasasawa and Semba [8] have suggested a possible explanation by their data on alloys of α -manganese with transition metal impurities. The results of Nagasawa and Semba [8] showed a low temperature resistivity minimum in the neighbourhood of 15 K and below this temperature the resistivity obeyed a T^2 , law suggesting spin fluctuation scattering.

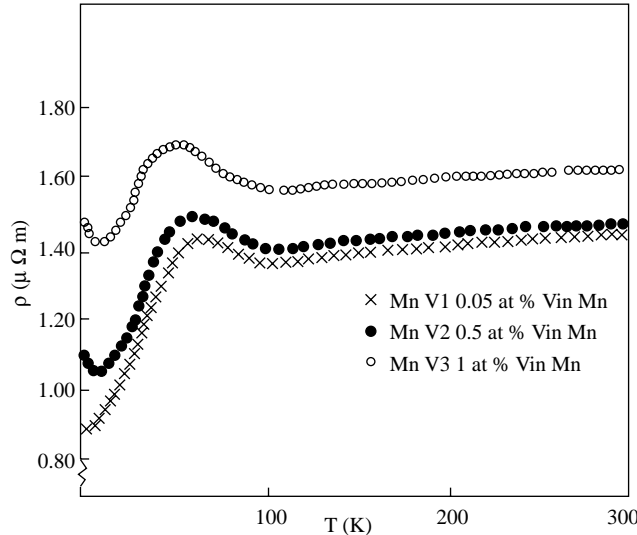


Figure 1. Electrical resistivity as a function of temperature for each of the samples MnV1, MnV2 and MnV3.

Murayama and Nagasawa have given the following expression for the resistivity in a transverse and longitudinal applied field at very low temperatures [14]:

$$\rho(B, T) = \rho_o(B) + A(B)T^2.$$

Here, $\rho_o(B)$ is the residual resistivity in the presence of magnetic field B . The second term is the spin fluctuation term, containing the coefficient, and is dependent on B . For the present investigation, in the absence of an applied magnetic field, the expression can be written as

$$\rho(T) = \rho_o + AT^2.$$

Figures 2(a, b, c) illustrate the dependence of the electrical resistivity on T^2 for samples MnV1, MnV2 and MnV3, respectively, below 10 K. In all cases the resistivity obeys a T^2 law suggesting that the vanadium impurities in the manganese films gives rise to a distortion of the magnetic moment of the manganese atoms

and thus leading to spin fluctuation scattering of the conduction electrons. It is also observed that the coefficient of T^2 is positive for MnV1 whilst those of MnV2 and MnV3 are negative. This is consistent with the results of Nagasawa and Semba [8] for the change in the sign of the coefficient of T^2 in some of these alloys containing V, Co, and Ni impurities. In each case, referring to Figure 2, the resistivity deviates from a T^2 law at about 7 K. The residual resistivities of these samples are what one might expect from Matthiessen's rule.

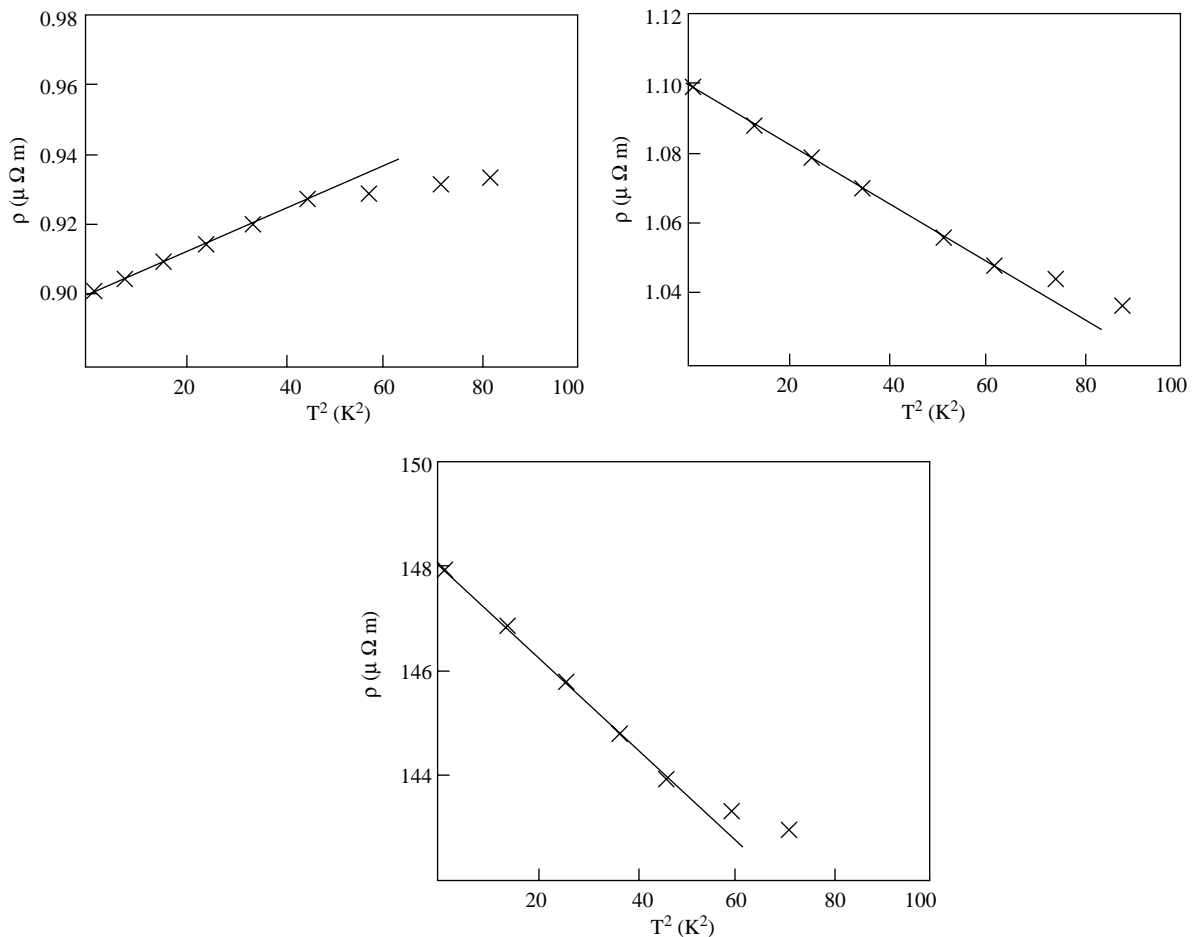


Figure 2. Electrical resistivity as a function of the square of temperature, T^2 , $T < 10$ °C, for (a) sample MnV1, (b) sample MnV2 and (c) sample MnV3.

Within the context of previous studies [15] in Mn-Cr alloys, the room temperature resistivities (ρ_{300}) are comparable to those of Mn-Cr alloys. The residual resistivities ρ_0 are also comparable in order of magnitude. Cr and V are all in the transition series, with Cr following vanadium; consequently, the magnitude of the resistivities might have something to do with the electronic structure of the impurities, namely vanadium and chromium.

4. The Néel Point of MnV thin Films

Whittaker et al [16], Williams and Stanford [17] have made an attempt to understand the nature of the complex magnetic interaction in antiferromagnetic α -Mn by determining the Néel point of bulk α -Mn and its alloys. They define the Néel point as corresponding to the first minimum on the resistivity temperature

curve. This is in contradiction with magnetic scaling theory. Zunsteg and Parks [18] have defined the Néel point 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 Goldberg [11] have suggested that the anomaly in the temperature derivative of the resistivity ($d\rho/dT$) 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 hydrodynamic-critical transition is defined by the position of the singularity in the temperature derivative of the resistivity versus temperature. Consequently, a plot of the temperature derivative ($d\rho/dT$) against temperature defines the Néel point T_N in antiferromagnetic materials. The slope of the ρ - T curve for these curves was calculated by drawing a straight line through four adjacent points and the slope calculated from the average temperature of the four points.

Figures 3(a, b, c) show the electrical resistivity and its temperature-dependent differential as a function of temperature for samples MnV1, MnV2 and MnV3. One can easily see the Néel points of samples MnV1, MnV2 and MnV3 are clearly established by the spikes at $T_N = 86, 82$ and 72 °C, respectively, suggesting a shift of T_N to lower values as the concentration of vanadium is increased in the sample; hence T_N might depend upon the nature and amount of impurity in Mn. A summary of the results together with those of Boakye et al [15] is given in Table 1. The present measurements of T_N in MnV alloys are consistent with those of MnCr alloys, which also exhibits shift of T_N to lower values. Again, these results might have something to do with the electronic structure of the nature of the impurity.

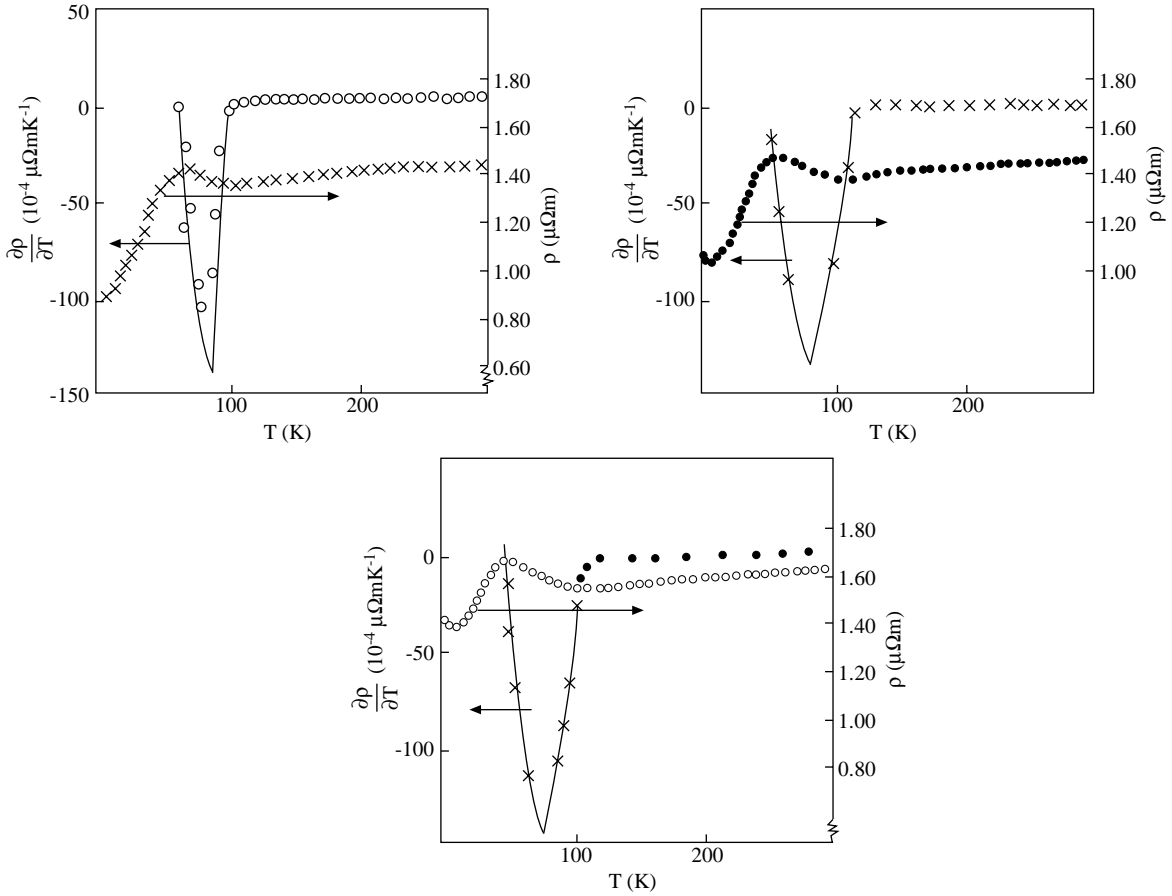


Figure 3. Electrical resistivity and its temperature-dependent differential, as a function of temperature for (a) sample MnV1, (b) sample MnV2 and (c) sample MnV3.

Table. Resistivity of Mn-V thin films. The last two are for comparison with Mn-Cr compositions.

Sample	Film thickness (Å)	ρ_{300} ($\mu\Omega\text{m}$)	ρ_0 ($\mu\Omega\text{m}$)	T_{min1} (K)	T_{min2} (K)	T_{max} (K)	Slope at 300 K ($\Omega\text{m K}^{-1}$)	T_N (K)	Coefficient of T^2 ($\mu\Omega\text{m K}^{-2}$)
Mn V1	2400	1.48	0.90	95	-	70	2.80×10^{-4}	86 ± 1	6.20×10^{-4}
Mn V2	3000	1.50	1.10	100	10	60	2.75×10^{-4}	82 ± 1	-8.00×10^{-4}
Mn V3	2000	1.60	1.48	105	12	50	2.60×10^{-4}	72 ± 1	-10.00×10^{-4}
0.5 at % Cr in Mn after Boakye et al. [15]	2000	1.52	0.92	90	-	71	2.85×10^{-4}	83 ± 1	11.00×10^{-4}
1.0 at % Cr in Mn after Boakye et al. [15]	2400	1.60	1.39	95	10	69	2.60×10^{-4}	79 ± 1	-7.00×10^{-4}

5. Conclusion

The present results indicate that the Néel point of thin film of Mn-V alloys decrease with increasing vanadium concentration. The low temperature resistivity of these samples obey a T^2 law, indicating a spin fluctuation scattering mechanism in the films.

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