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THE ELECTRICAL RESISTIVITY OF SEVERAL DILUTE
ANTIFERROMAGNETIC ALLOYS OF α -MANGANESE

M. S. Thesis Submitted to Iowa State University,
May 1972

W. Williams, Jr.

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DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

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R5303

The electrical resistivity of several dilute
antiferromagnetic alloys of α -manganese

by

Willie Williams Jr.

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Physics
Major: Solid State Physics

Approved:

John L. Stanford
In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1972

R5303

TABLE OF CONTENTS

	Page
ABSTRACT	v
INTRODUCTION	1
APPARATUS	10
EXPERIMENTAL TECHNIQUES	17
Sample Preparation	17
Procedure	18
RESULTS AND DISCUSSION	21
Mn-Fe	25
Mn-Ru	27
Mn-Cr	29
Mn-V	33
CONCLUDING REMARKS	42
LITERATURE CITED	45
ACKNOWLEDGMENTS	46

ABSTRACT

Electrical resistivity measurements have been made on several dilute alloys of antiferromagnetic α -Mn. The measurements were made on manganese-rich Mn-Fe, Mn-Ru, Mn-Cr and Mn-V with percentages of solute varying from 1 atomic percent up to 3 atomic percent. These measurements were undertaken to provide some understanding of the complex antiferromagnetic nature of Mn.

Since Mn, as well as Mn-alloys, exhibits anomalies in the temperature dependence of the resistivity at the onset of antiferromagnetic ordering, the Néel temperatures of the alloys have been determined. The experimental results show that dissolving Fe or Ru into solute with Mn tends to raise observed Néel temperature, while dissolving Cr or V depresses the Néel temperature. With the introduction of these impurity elements into α -Mn, an initial rate of change in T_N of +14, +16, -14, and -20 degrees Kelvin per atomic percent solute are observed for Fe, Ru, Cr, and V respectively.

These results are consistent with a study by Bellau and Coles (1) and seem to support a large spin-disorder resistance above the Néel temperature.

LIST OF FIGURES

	Page
Figure 1. One half of the unit cell of Alpha Manganese. The nearest neighbors of type 1 atom are shown. This group of 29 atoms is repeated at each corner and body-centered position in the cubic lattice	7
Figure 2. The sample holder assembly showing the sample holder and vacuum jacket	11
Figure 3. Block diagram of the apparatus used in resistivity measurements	15
Figure 4. A portion of the periodic table which shows the relative position of the element used in this study	24
Figure 5. The electrical resistivity of Mn-1 at. % Fe and Mn-2.7 at. % Fe as a function of temperature	26
Figure 6. The electrical resistivity of Mn-0.89 at. % Ru and Mn-2.40 at. % Ru as a function of temperature	28
Figure 7. The electrical resistivity of Mn-1.9 at. % Cr as a function of temperature	31
Figure 8. The electrical resistivity of Mn-2.7 at. % Cr as a function of temperature	32
Figure 9. The electrical resistivity of Mn-1 at. % V as a function of temperature	34
Figure 10. The normalized electrical resistivity of Mn-1.9 at. % Cr and Mn-2.1 at. % V as a function of temperature	36
Figure 11. The electrical resistivity of Mn-2.4 at. % V as a function of temperature	38
Figure 12. The Neel temperature as a function of concentration in Mn alloys	40

LIST OF TABLES

	Page
TABLE I. Summary of the four phase transitions in manganese.	5
TABLE II. Magnetic moments determined for a collinear spin model.	8
TABLE III. Chemical analysis of % of solute present	21

INTRODUCTION

The ability of a metal to conduct electricity is one of its main distinguishing characteristics. Its ability to conduct in the presence of an electric field is due to a large number of quasi-free electrons. Since electrons are not tightly bound they have the ability to move through the lattice. If it were not for disturbing affects that tend to impede this motion, the conductivity of a metal would be infinite. However, in all real metals, there are always disturbing affects that impede the electrons motion, scattering them and giving rise to a resistance known as the electrical resistance.

If the dimensions of the metal sample are known, the resistivity of the metal may be calculated from voltage and current measurements. To see this, consider a conductor of uniform cross sectional area A and length ℓ , in which a voltage V between its ends is produced by a current I . We have the relations:

$$E = \frac{V}{\ell} \quad \text{and} \quad J = \frac{I}{A} \quad (1)$$

Ohm's Law gives

$$\frac{J}{E} = \frac{I}{\rho} \quad (2)$$

where ρ is the resistivity. Combining equations 1 and 2, we have

$$\rho = \frac{V}{I} \frac{A}{\ell} \quad (3)$$

ρ will be a particular value for a given material. This value of the resistivity will depend on the temperature and pressure at any instant, as well as the chemical and physical conditions of the metal sample itself.

By chemical condition, we refer to the type and proportions of foreign-impurity atoms present. Their effect on the resistivity will depend not only on the quality and quantity of the impurity atom but also on the way in which they are distributed in the lattice--for example, whether they are in solid solution, ordered in sublattices, or present in clusters or as compounds. The physical condition of the sample refers to imperfections in the lattice, which arise from localized strains. These strains may be caused by dislocation, vacancies, or interstitial atoms. Thus the physical condition depends very much on the previous history of the sample, as for example, whether the sample has been subject to cold work, irradiation, or annealing. Also the temperature dependence is more than just modifying the extent of lattice vibrations, since crystallographic phase changes and magnetic transitions or other order-disorder phenomena may

also result.

Thus in general the resistivity, ρ is a function of temperature. However, at very low temperatures the resistivity approaches a constant value known as the residual resistivity, ρ_0 . This residual resistivity arises from impurities defects, and strains in the sample. For a pure, annealed metal, ρ_0 is only a small fraction of the total resistivity at room temperature.

The separation of the resistivity into a temperature-dependent part, intrinsic resistivity (ρ_{iT}) and a temperature-independent part, ρ_0 is known as Matthiessen's rule and is written

$$\rho = \rho_0 + \rho_{iT} \quad (4)$$

Another important contribution to the resistivity that occurs only in ferromagnetic and antiferromagnetic metals below their magnetic transition temperature is due to scattering from a disordered spin arrangement. The magnitude of this effect varies according to the element. This magnetic disorder spin term, ρ_{mT} is temperature dependent below the Curie or Neel temperature. This contribution may be considered to a first approximation additive to the residual and intrinsic resistivity. Thus we have

$$\rho = \rho_0 + \rho_{iT} + \rho_{mT} \quad (5)$$

One such interesting transition metal is manganese. It is a complex antiferromagnetic metal in the first long series. Its atomic number is 25 and it has an atomic weight of 54.94.

In the free-atom state, the transition elements beginning with scandium to nickel in the first long series are a group of elements in which the energies of the electrons in the 4s and 3d states are not very much different. The tendency is for 1 or 2 electrons to be in the 4s band and those in the 3d band to increase from one for scandium (atomic number 21) to eight for nickel (atomic number 28). The electronic structure of the free Mn atoms is

However, in the metallic state, the structure of the third and fourth quantum shell are somewhat more complex.

The transition metals tend to have a very high value of electrical resistivity and specific heat. In the case of Mn, the intrinsic resistivity, (ρ_{iT}) (2) and electronic specific heat coefficient (3) are 150 μ -ohm-cm and 28×10^{-4} cal/mol/deg² respectively at room temperature. In order to explain these observed phenomena, interactions between the 3d and 4s shells are postulated.

Mn has four crystallogical phase transitions. Of these four, most of the experimental work has been done on the α - and β -phases. The four phases are summarized in Table I. (4)

TABLE I. Summary of the four phase transitions in manganese.

Phase	Structure	Lattice Constant	Number Of Atoms/Cell	Phase Change Temperature
α	Cubic	$a=8.9135 \text{ \AA}$	58	727°C
β	Cubic	$a=6.3037 \text{ \AA}$	20	1095°C
γ {	High temperature Face centered cubic	$a=3.864-3.868 \text{ \AA}$	4	1133°C
	Room temperature (Alloy only) Face centered tetragonal	$a=3.784 \text{ \AA}$ $c/a=0.940$	4	
δ {	At 1140°C Body centered cubic	$a=3.081 \text{ \AA}$	2	1244°C
	Melting point Body centered cubic	$a=3.094 \text{ \AA}$		

This study was concerned only with the α -phase. α -Mn has a cubic structure with 58 atoms to the unit cell. Earlier work by Bradley and Thewlis (5) showed that the structure contained four kinds of atoms.

The basis of the whole arrangement is a simple body-centered cubic lattice, with each lattice point being associated with a cluster of 29 atoms. Figure 1 shows one such cluster of atoms around the central atom of the unit cell.

Around each type 1 atom is an octahedron of type 4 atoms, the opposite faces of the octahedron being of different sizes so that the symmetry is tetrahedral. The four type 2 atoms are somewhat further from the center of the group and are arranged tetrahedrally about the center. The twelve outer-most type 3 atoms comprise a polyhedron having cubic and octahedral faces. The whole cluster has symmetry which is tetrahedral, as is that of the crystal as a whole.

Several neutron diffraction (6,7) investigations of the magnetic structure of α -Mn have been done. These studies have shown that each of the four atom sites have different magnetic moments. The results of a recent study by Oberteuffer (8) is summarized in Table II. The Oberteuffer study, as well as an early one by Shull and Wilkinson (6), established the existence of an antiferro-

Figure 1. One half of the unit cell of Alpha Manganese. The nearest neighbors of type 1 atom are shown. This group of 29 atoms is repeated at each corner and body-centered position in the cubic lattice.

magnetic state in α -Mn. This state appears to set in around 95°K. Below this temperature, Mn becomes anti-ferromagnetic.

TABLE II. Magnetic moments determined for a collinear spin model.

Magnetic Moment	77°K	50°K	4°K
I	1.25 μ_B	1.54 μ_B	1.72 μ_B
II	0.95 μ_B	1.14 μ_B	1.46 μ_B
III	-0.82 μ_B	-0.97 μ_B	-1.11 μ_B
IV	-0.04 μ_B	-0.05 μ_B	0.02 μ_B

It has been shown by Bellau and Coles (1) that pure Mn exhibits a sharp cusp in its resistivity curve around 95°K. It should be noted that this temperature corresponds to the temperature at which antiferromagnetism sets in as reported in the neutron diffraction studies. Thus this minimum is thought to be associated with the ordering temperature, T_N .

In studying polycrystalline Mn alloys, the temperature dependence of this type cusps was observed to depend on the amount and type of impurities in the sample. Bellau and Coles (1) has shown that iron tends to raise the Néel temperature, while chromium tends to suppress it. Coles has suggested that such changes in the resistance curve can be explained by the

presence of a large spin-disorder resistance above the Neel temperature, so cooling through this temperature will produce a reduction in the spin-disorder scattering and at the same time a change in the conduction electron configuration.

The purpose of this work is to systematically study the nature of the change in the structure of the resistivity curve of Mn with the addition of small percentages of impurities. This investigation was conducted using up to 2.5 atomic percent impurity concentrations, with impurity elements both to the right (Fe,Ru) and left (Cr,V) of manganese in the periodic table.

APPARATUS

A glass dewar system was employed for containment of cryogenic fluids. The system consisted of an inner helium dewar surrounded by an outer nitrogen dewar. This provided a temperature range from about 4.2°K to 300°K . The standard four probe technique was used for the resistivity measurements.

The sample holder consisted of a 20.5 in. piece of thin-wall stainless steel tubing attached at one end to a 4 11/16 in. diameter brass plate, provided with an opening for the transfer and recovery of cryogenic fluids. The other end was attached to a 5 1/2 in. sythane rod. A flat section was milled into the lower part of the rod and a 2 9/16 in. X 1/2 in. X 1/4 in. copper plate was mounted on the rod. This plate was used to provide a uniform temperature for the samples, and to provide a heat sink for the current and voltage leads. One end of the copper plate was milled to accept a heating element. The heating element consisted of 21 ft. of 4.61 ohm per foot Manganin wire. The wire was carefully doubled and twisted together before winding and gluing it to the heater block. This was done to eliminate any induced voltages that might appear in the samples as a result of the heater. G. E. #7031 varnish was used to glue the heater to the block.

Figure 2. The sample holder assembly showing the sample holder and vacuum jacket

The sample holder could accommodate five samples at any given time. Just above the sythane-stainless connection, one section of a Ultek vacuum valve was soldered to the stainless tube with the aid of a copper adapter piece. The other section of this valve was soldered to another thin-wall stainless tube ($\sim \frac{1}{8}$ in.) which served as a vacuum jacket. This arrangement allowed the entire sythane section to be enclosed within a vacuum by slipping it into the vacuum jacket. The vacuum seal was accomplished by a copper gasket placed between the two sections of the valve and tightened into place by bolts located in a section of the outer circumference of the valve. (See figure 2).

All leads were thermally anchored to the copper plate and to the bath by gluing all leads to the inside of the copper adapter section of the vacuum jacket with G. E. #7031 varnish. All leads passed up the inside of the stainless tubing to the top of the sample holder. After experimenting a bit with conax fittings with little success in maintaining a vacuum tight system, two methods were finally used to extract the leads. These leads, such as current and heater leads, were attached to the back of a nine pin feed-through which had been soldered in place. Plug-in connections could then be used to connect these leads to the external apparatus. For those leads which could not be broken, such as thermocouples and voltage leads,

an Epoxy feed-through was used. This consisted of drilling small holes in a nylon rod to provide exits for the leads. Once the leads were through, Epoxy was used to seal off the small holes and securely anchor the nylon plug into an acceptor fitting at the top of the stainless tube.

The top of the sample holder was also provided with a type 505 thermocouple pressure gauge and an opening through which a vacuum could be maintained inside the sample holder. The vacuum opening was connected by hose to an exchange gas system. This system allowed a small amount of exchange gas to be introduced during cooling and also during heating to insure a uniform temperature inside the vacuum jacket. Helium was used as the exchange gas.

The temperature was measured using a Gold-Iron thermocouple in the region between 4.2°K and 40°K . In the region between 40°K and room temperature, a copper-constantan thermocouple was used. In the case of the Gold-Iron thermocouple, some difficulty arises in trying to form the thermocouple junction by soldering. This junction was finally achieved by melting the wires together in a flame. Both thermocouples were glued to the copper plate with G. E. #7031 varnish. These thermocouples were fed up to the usual ice bath and from there to a Leeds and Northrup K-4 potentiometer with a sensitivity of $0.5\mu\text{V}$. This was coupled with a Keithley model 155 null detector to complete the temperature

measurement system. The detector had a sensitivity of $.02 \mu V$.

To insure almost constant and uniform temperature, the heater was connected to an automatic temperature-controller. The incorporation of this control into the system not only provides more or less constant temperatures, but also minimizes the time required to achieve a desired temperature to within two degrees by merely setting that temperature on the controller.

The sensing device in the control was a copper-constantan thermocouple, that was glued with G. E. #7031 varnish to the heater coil. This voltage from the thermocouple was then balanced against a preset voltage (corresponding to the desired temperature) on the control. The control would automatically adjust the heating element until the temperature of the system was at the preset temperature, thus achieving a null. The control would maintain that condition until a new temperature was preset.

Since the system was designed to accommodate five samples simultaneously, it was necessary to provide five separate pairs of voltage leads. Number 32 copper wire was used for the voltage leads. These leads were fed through an Epoxy fitting and anchored in an ice bath to insure uniform temperature across the connections to the external measuring apparatus. A Leeds and Northrup K-5 potentiometer

Figure 3. Block diagram of the apparatus used in resistivity measurements

was used to measure the voltages across the samples. The K-5 had a sensitivity of $.02 \mu\text{V}$. The potentiometer was nulled using a second Keithley model 155 null detector.

Because of the number of samples being studied simultaneously, it was necessary to incorporate a switch that would allow each sample in turn to be monitored. This was achieved by connecting the voltage leads to a Leeds and Northrup low-thermal double-pole rotary selector switch. This switch has 12 positions, thus allowing the switch to be wired for both forward and reverse voltage readings. This switch is rated to have less than $1.0 \mu\text{V}$ thermal emf and contact resistance of 0.001 ohm ($\pm 0.0005 \text{ ohm}$).

To insure the same current and to eliminate some of the leads, the samples were wired in series. A standard 1 ohm resistor was also placed in series with the samples. The voltage drop across the standard resistor could be used to monitor the current. Since this would require a third potentiometer, both the voltage drop across the standard resistor and the temperature were monitored on the same K-4 potentiometer. This was accomplished by using a second double-pole Leeds and Northrup low-thermal switch. The current was supplied by a Power Designs model 4005 constant current power supply. The supply was rated to have less than 0.1% or 250 microampers drift per hour.

EXPERIMENTAL TECHNIQUES

Sample Preparation

α -Mn is a very brittle substance and fabricating samples of suitable size and dimensions is often very difficult. These difficulties were made apparent throughout our sample preparation. Spark erosion processes, used in cutting the samples, usually left the samples cracked, if not completely broken. Even in cases where uncracked samples were available after spark erosion, the annealing processes often introduced small cracks in the samples.

Work with Mn is further complicated since Mn oxidizes quite readily. This complication becomes apparent in the attachment of leads. A thin layer of oxide on the surface is sufficient to provide a large contact resistance. This is significantly important in the attachment of potential leads.

A final consideration is absorption of hydrogen by Mn. This absorption of hydrogen can greatly enhance the observed resistivity. Thus, it is necessary to insure that the samples are not exposed to the atmosphere for any long period of time.

Samples were prepared from 99.99% high purity Mn flakes as quoted by Johnson Matthey. The following alloy systems were prepared: Mn-Cr, Mn-Fe, Mn-V, and Mn-Ru.

The Mn flakes, as received, were etched in dilute HCl to remove excess oxidation. These flakes were used to produce the Mn alloys.

The alloys were arc-melted into buttons about 3 cm in diameter. A slice was removed from the center section of each button by spark erosion. This slice, once obtained, was farther sparked-cut into parallelopipeds of approximate dimensions 2 cm X 1 mm X 1 mm.

Once samples of the desired dimensions were obtained, they were annealed in continuous vacuum for 6 hours at 620°C. Care was taken to insure that the annealing temperature did not carry the sample into the β -phase but yet at a temperature that would insure the removal of most of the strains.

Procedure

Once samples of suitable size had been cut and annealed, the voltage and current leads were attached. After trying several unsuccessfully methods, leads were finally attached by soldering with an ultrasonic soldering iron. Pure indium solder was used. The major difficulty in attaching the leads was that a thin film of oxidation covered the sample's surface. The ultrasonic soldering iron removed most of this oxidation, thus providing a clean surface. Care was taken to insure that the sample's voltage leads were sufficiently far from the current leads, so end effects would be negligible.

Each sample was mounted in turn on the copper plate of the sample holder. This was done with a thin film of G. E. #7031 varnish. This provided good electrical isolation, while still providing good thermal contact with the copper plate.

The entire sample support was placed inside the vacuum jacket and allowed to pump down to a pressure of 20 microns. Meanwhile, the voltage, current, and thermocouples leads, were connected to the external apparatus for a room temperature check. Once the above pressure was obtained, liquid nitrogen was transferred to the outer dewar. The entire system was allowed to reach nitrogen temperature before the inner dewar was filled with liquid helium. The final temperature of the system was near 4.2°K .

Once this temperature was reached, a small amount of exchange gas was introduced to insure a uniform temperature within the sample chamber before potential measurements were made. A 100 millampere current was passed through the samples and each sample's potential, as well as temperature, was monitored in turn. The potential across the standard resistor was also monitored to determine accurately the current through the sample. The temperature could be determined to within a tenth of a degree from a voltage-temperature conversion table predetermined to match the calibration of the thermocouples being used.

This procedure was repeated at intervals of $2-5^{\circ}\text{K}$ over the entire temperature range.

After the completion of measurements on a sample, a traveling microscope was used to determine the cross sectional area of the samples and the distance, ℓ , between potential leads. Equation 3, was used to calculate the resistivity of the various samples. Because the potential leads were soldered on, there was an uncertainty of $\sim 10-20\%$ in the measurement of the ℓ values. Consequently, the absolute resistivity values are not known to be better than $\sim 10-20\%$ accuracy.

RESULTS AND DISCUSSION

Three series of resistivity measurements were made on the following Mn alloy systems: Mn-Fe, Mn-Ru, Mn-Cr, and Mn-V. The percentage of solute present in each series is summarized below in table III. The results are believed to be correct to ± 0.1 at. %. The nominal purities of the material used were as follows: Cr-99.95%, V-99.95%, Ru-99.99%, Fe-99.95%, and Mn-99.99%.

TABLE III. Chemical analysis of % of solute present.

Mn Alloy	Series I	Series II	Series III
Cr	1.05	1.88	2.66
Fe	1.01	2.1	2.65
Ru	0.89	1.72	2.40
V	1.02	2.12	2.44

A mass spectroscopy analysis was also made to check for other impurities in the alloys. The results showed abnormally high amounts of Cu ($\sim 1,500$ ppm), C ($\sim 7,000$ ppm), and O ($\sim 1,000$ ppm). These contaminants were believed to be acquired primarily during the process of sample preparation and particularly, during spark erosion. Consequently, these contaminants would be only on the surface of the samples and

would not contribute to the observed effect caused by the introduced impurities. Since none of the samples were electropolished before annealing in this study, this would be a plausible explanation.

In a preliminary verification, several samples were prepared as before. These samples, along with several from the previous mass spectroscopy analysis, were carefully etched and electropolished. They were once again submitted for mass spectroscopy analysis. The results tended to support the idea of only surface contaminants Cu (< 100 ppm), C (< 50 ppm) and O ($\sim 10,000$). The apparent increase in O can be attributed to oxidation of the samples, since Mn oxides quite readily.

However, this mass spectroscopy analysis was made on unannealed samples, while the actual data were taken on annealed samples. It therefore, became necessary to verify whether annealing propagates the contaminants into the samples, before it could be conclusively determined that the samples contained only surface contaminants.

To verify this, samples were prepared as before. Several of the samples were annealed while the others were not. The annealed group was divided into two sub-groups. One sub-group was etched and electropolished after annealing, while the other was not. A similar subdivision was made with the unannealed samples.

The unannealed samples provided a necessary reference for comparison between annealed and unannealed samples.

All samples were submitted for mass spectroscopy. The analysis showed that both the annealed and unannealed samples that were not electropolished contained 3000 ppm or more Cu, while those annealed and unannealed samples that were electropolished showed a reduction in Cu by a factor of 100, i.e. less than 30 ppm Cu. Thus, the analysis tends to point toward surface contaminants only and therefore, those contaminants should not have influenced the observed bulk resistivity.

For the purpose of discussion and presentation of the resistivity data, each Mn alloy system will be discussed separately. Figure 4 shows the position of the impurity element in relationship to Mn in the Periodical Table. Cr and V have 1 and 2 less electrons per atom respectively, than Mn in their 3d shell. Fe, on the other hand, has one electron per atom more. Since Fe has a tendency to have localized moments of its own, Mn-Ru alloys were also considered to insure that any effect due to these moments might be determined by comparison with the Ru data.

As pointed out previously, α -Mn has a Neel temperature around 95°K; on cooling through this temperature, the resistivity falls less rapidly or increases. Any such observed departure from the high-temperature behavior of the

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

TRANSITION ELEMENTS

Figure 4. A portion of the periodic table which shows the relative position of the element used in this study

resistivity in the alloys will also be assumed to indicate the ordering temperature, T_N .

Mn-Fe

Upon dissolving 1 at. % Fe in α -Mn, we find the Neel temperature to be shifted 14°K . With 2.7 at. % Fe dissolved in α -Mn, the Neel temperature occurs at 132°K (an increase of 37°K). Figure 5 shows the resistivity of the 1 and 2.7 percent Mn-Fe alloys. The change in resistivity between room temperature and T_N is very small. The change is only about $6.5 \mu\text{ohm-cm}$ and $8 \mu\text{ohm-cm}$ for the 1 and 2.7 percent alloy, respectively. The behavior in this temperature range is almost identical to that of pure α -Mn.

After the minimum corresponding to the Neel temperature, there is a large enhancement of the resistivity that peaks around 70°K in both samples. The height of this peak, measured from the minimum, depends on the concentration. With increasing concentration, there is a corresponding increase in the height of this peak. The observed heights for the 1 and 2.7 percent samples were about $9.5 \mu\text{ohm-cm}$ and $19 \mu\text{ohm-cm}$ respectively.

After these peaks, the resistivity falls off rather sharply, the amount of decrease depending markedly on the amount of solute present. Of course, at first glance this is to be expected to some degree.

Figure 5. The electrical resistivity of Mn-1 at. % Fe and Mn-2.7 at. % Fe as a function of temperature

According to Matthiessen's rule, as the impurity is increased, the residual resistivity increases. However, a closer look suggests that the magnitudes of the changes are such that even at very low temperatures an additional mechanism must be at work. The change in the resistivity between room temperature and about 5°K is $71 \mu\text{ohm-cm}$ and $14 \mu\text{ohm-cm}$ for the 1 and 2.7 percent Mn-Fe alloys, respectively. On the basis of Matthiessen's rule alone, the introduction of only 2.7 percent impurities does not seem to reflect the observed large change in the resistivity at low temperatures but rather suggests that there is a large resistance due to other mechanisms.

This behavior might be expected if an Fe atom carrying a localized magnetic moment replaced one of the Mn atoms with little or no moment. There would be a corresponding elevation in T_N . As more and more of these Fe atoms replace Mn atoms, the modification of the antiferromagnetic Brillouin Zone would reduce the freedom of the conduction electrons. Thus, there would be a corresponding increase in the resistivity.

Mn-Ru

The most noticeable feature of the Mn-Ru data is the striking resemblance to that of the Mn-Fe data. Figure 6 shows the resistivity data for the 1% and 2.4% Mn-Ru samples.

Figure 6. The electrical resistivity of Mn-0.89 at. % Ru and Mn-2.40 at. % Ru as a function of temperature

The Mn-1 at. % Ru sample showed an ordering temperature around 111°K. The 2.4 at. % Ru sample ordered around 135°K. There is very little change in the resistivity from room temperature to the Neel temperature. The 2.4 at. % Ru sample changed only 3 μ ohm-cm, while the 1 at. % Ru sample changed by 5 μ ohm-cm. As was observed in the Mn-Fe alloy samples, there is an enhancement in the resistivity below the Neel temperature. The resistivity reaches a peak around 70°K. The height of the peaks were 19 μ ohm-cm, and 11 μ ohm-cm for the 2.4 and 1 at. % Ru samples, respectively.

The amount of change in the resistivity between 5°K and room temperature, as observed in the Mn-Fe alloy samples, depends on the amount of solute present. The change in the resistivity over this temperature range is about 9.5 μ ohm-cm and 63 μ ohm-cm for the 3 and 1 at. % Ru samples, respectively. The close similarity between the structure of the Mn-Fe and Mn-Ru data suggest that the contribution to the observed affect from possible localize moments in Fe is little or none (assuming Ru atoms in Mn do not have local moments). The fact that Fe and Ru both have partially filled shells containing one additional electron per atom more than Mn suggests that the observed affect is of an electronic nature.

Mn-Cr

The introduction of Cr into Mn has just the reverse affect from Fe and Ru. The Neel temperature is suppressed

or lowered. The Mn-1.9 at. % Cr sample exhibits the most structure in the resistivity versus temperature plot and is shown in Figure 7. This sample exhibits the more or less constant value of ρ above 220°K as observed in the Fe and Ru samples. The Néel temperature is shifted down 28°K from the value observed in pure Mn, T_N occurring at 72°K for the Mn-2 at. % Cr sample. Below the Néel temperature, the resistivity reaches a small peak and falls off. This behavior follows that of pure Mn. The height of the peak is about $2.5 \mu\text{ohm-cm}$ and is centered about 55°K . The change in ρ between room temperature and 5°K is about $33 \mu\text{ohm-cm}$. The resistivity data for the addition of Cr to Mn suggest that Cr reduces the spin-disorder resistance. This suggests that Cr additions diminish the magnitudes of the localized moments in Mn.

The 1 and 2.7 at. % Cr samples do not exhibit as much of an anomaly in their resistivity versus temperature data as does the 2 at. % Cr sample. However, both the 1 and 2.7 at. % Cr additions to Mn diminish the ordering temperature. The resistivity data for 2.7 at. % Cr in Mn is shown in Figure 8. There is no apparent minimum in the curve. There is an inflection point around 55°K . This was taken as the ordering temperature. Extrapolation of the resistivity curve to room temperature gives a change in ρ of about $66 \mu\text{ohm-cm}$. From the 1.9 and 2.7 at. % Cr data, there appears to be a

Figure 7. The electrical resistivity of Mn-1.9 at. % Cr as a function of temperature

Figure 8. The electrical resistivity of Mn-2.7 at. % Cr as a function of temperature

progressive increase in the change of ρ between 5°K and room temperature. This once again suggest that as impurity scattering increases there is a corresponding decrease in spin-disorder scattering. The Mn 1 at. % Cr sample exhibits a slight inflection around 81°K. This was also taken as the Neel temperature.

Mn-V

Dissolving V in Mn, like Cr, lowers or suppresses the Neel temperature. But unlike the Mn-Cr data, all the V samples have broad anomalies associated with the ordering temperature. The resistivity data for Mn-1 at. % V is shown in Figure 9. There is a broad minimum in the resistivity at 65°K. The resistivity increases about 6 μ ohm-cm to a broad maximum around 25°K. After this maximum, the resistivity drops slightly to a secondary minimum around 18°K. The resistivity thereafter tends to increase. This secondary minimum anomaly was observed only in the 1 at. % V sample. The structure was reproducible and seems to be a real affect. Whittaker et al.(9), in a recent paper, has reported a secondary minimum in α -Mn and several dilute Mn alloys below 20°K. The data does not suggest any immediate probable cause. However, most of the Mn-alloys are very sensitive to strains. A first explanation might be that the secondary minimum is due to physical strains in the sample.

Figure 9. The electrical resistivity of Mn-1 at. % V as a function of temperature

A second noticeable difference in the Mn-V data is that for temperature below the ordering temperature there is no apparent appreciable decrease in the resistivity. In fact, there is a slight increase in the resistivity below the ordering temperature. As was suggested for the Mn-Cr alloys, the Mn-V data appear to suggest that the addition of V diminishes the localized moments on the Mn atoms. However, the antiferromagnetic Brillouin zone planes modify the electronic structure in such a way as to increase the resistance.

The normalized resistivity data for Mn-2 at. % V is shown in Figure 10. The resistivity curve exhibits the same general structure as observed in the 1 at. % V sample. The resistivity drops off as a function of temperature, reaching a broad minimum that is centered around 45°K. After this minimum, the resistivity tends to increase, with no apparent indication of falling off even at lower temperatures. To contrast this behavior with that of Cr, Figure 10 also includes the normalized resistivity data for Mn-2 at. % Cr. The high temperature behavior above the Néel temperature is very similar, with the Mn-V sample falling off slightly faster than the Mn-Cr sample.

However, for the same atomic percent concentration of V as Cr, introducing V approximately doubles the observed Néel temperature shift caused by introducing Cr.

Figure 10. The normalized electrical resistivity of Mn-1.9 at. % Cr and Mn-2.1 at. % V as a function of temperature

Another interesting point about these two binary systems is the observed maximum in the Cr sample below the ordering temperature, and the apparent absence of such a maximum in the V sample.

If we assume that the observed increase in the resistivity below the Néel temperature is due to modification of the Brillouin zone planes caused by the onset of antiferromagnetism, it would appear that in Mn-V, the antiferromagnetic Brillouin zone planes produce such a severe reduction in the freedom of the conduction electrons that even a reduction in the spin-disorder resistivity cannot compensate for the resistance resulting from the formation of new zones.

Figure 11 shows the normalized resistivity for Mn-2.4 at. % V. These data seem to strongly suggest that 2.4 at. % V in Mn removes much of the spin-disorder resistance, but the absolute resistivity values are too uncertain to be absolutely sure.

As a final note of discussion, it seems noteworthy to consider for a moment the ordering temperature associated with each of the alloy systems. It would appear that the observed shifts in the alloy's Néel temperature from that for pure Mn is revealing information about the mechanism at work in causing the antiferromagnetic state in Mn.

However, before summarizing the observed Néel temperatures, a note on their choice is in order.

Figure 11. The electrical resistivity of Mn-2.4 at. % V as a function of temperature

There are some difficulties associated with determining their values. This is apparent from considering figure 7, the resistivity of Mn-2.7 at. % Cr. In this case, there is no apparent minimum, only an inflection in the curve. There are no standard procedures for the choice of T_N . In the case of α -Mn, this choice has been the temperature corresponding to the minimum in the resistivity curve. But even in the case where there is a minimum in the resistivity curve, often the minimum is broad, with a span of 3 or 4 degrees (see figure 8, Mn-1 at. % V). So the choice really becomes difficult in cases where there is only an inflection in the $\rho(T)$ curve.

For the present work, the following guidelines were used. For the curves exhibiting broad minima, T_N was taken at the center of the minimum. For curves exhibiting only inflections, T_N was taken to be the point of inflection. With this guideline, Figure 12 summarizes the data. The T_N values are thought to be correct to $\pm 2^\circ\text{K}$.

Alloys with Fe or Ru, which are to the right of Mn in the Periodic Table and having one electron per atom more than Mn in their partially filled shells, tend to increase T_N . There appears to be a linear relationship between T_N and the amount of solute introduced. These data show this to be true up to 2.7 and 2.4 at. % Fe and Ru, respectively. In the case of Cr, which is to the left of Mn and has one less

Figure 12. The Néel temperature as a function of concentration in Mn alloys

electron per atom than Mn, the Neel temperature is suppressed. The relationship appears to be linear up to 2.6 at. % Cr. Finally with V, also to the left of Mn and having two less electrons per atom than Mn, the Neel temperature is again suppressed. However, the latter alloys tend toward a quadratic relationship between T_N and the amount of solute.

CONCLUDING REMARKS

This manuscript reports the results of resistivity measurements on several dilute alloys of α -Mn. These results along with others, (1, 10, 11) give preliminary data on the behavior of the antiferromagnetic transition in α -Mn. A resistance minimum, a notable characteristic reported of pure α -Mn, (12) was also present in some of the alloys. The temperature T_N at which this resistance minimum occurred was shifted according to the valency difference between the impurity and the host metal. V and Cr (lower valency) caused T_N to decrease while Fe and Ru (higher valency) caused T_N to increase. A somewhat similar behavior is observed in Cr-rich alloys (13). The data clearly point out that the dependence of T_N and the general structure of the resistivity curve depend on the amount of solute in Mn. Also, they appear to depend markedly on the type of solute. This dependence appears to be closely linked to the valence of the introduced metal atoms. Perhaps equally clear is the fact that Matthiessen's rule was not obeyed in any of the alloys.

In light of some of the observed effects, the resistivity data lead to the following considerations. It would appear that the large value of ρ for α -Mn is due to spin-disorder scattering and upon cooling through the Neel temperature this type of scattering is reduced. The small

increase in the resistivity below T_N is due to new restrictions imposed on the conduction electrons because of the new magnetic Brillouin zones. Thereafter the resistivity falls off with temperature somewhat like an ordinary metal. The introduction of impurity elements with valence greater than Mn seem to contribute to the spin-disorder resistance and further complicate the restriction imposed by the antiferromagnetic Brillouin zones. This behavior seems to be reflected in both the Mn-Ru and Mn-Fe data. However, unlike α -Mn, the Mn-Fe and Ru alloys do not fall off appreciably at low temperatures. Whether the large ρ at low temperature could be due to local magnetic moments on Fe and Ru atoms or not is not known. However, the data certainly suggest that whatever ordering occurs in α -Mn at low temperature, is inhibited in the Mn-Fe and Mn-Ru samples.

With the introduction of impurity elements with valence less than that of Mn, the data appear to reflect a lowering of the spin-disorder resistance as well as reducing the resistance due to the antiferromagnetic Brillouin zone. This behavior is reflected throughout the Mn-V and Mn-Cr data. These impurity elements appear to contribute a considerable degree of spin-disordering at high temperatures. However, the lack of an appreciable decrease in the resist- (in fact a slight increase in Mn-V) below T_N suggests that there are significant contributions to the resistance other

than just impurity scattering.

Measurements that might be of future interest are the study of higher atomic percentages of the alloy systems studied in this manuscript. Such data would provide information on whether or not there is a critical concentration of impurity atoms above which there is little or no change produced by farther additions. Information on such concentration should provide some small clue concerning the nature of the transition. Measurements of other binary systems like Mn-Re and Mn-Mo should lead to even further insights. Ternary systems like Mn-Cr-Fe or Mn-Mo-Ru would certainly be of interest to study.

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ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Dr. John Stanford for suggesting this topic and for the guidance and inspiration he provided during the course of this study.

A special acknowledgment to the members of Dr. Stanford's research group and many other members of the Physics department, too numerous to mention, for the vast resources they provided. Also I would like to thank Mr. F. A. Schmidt for providing the alloys in this study.

I wish to express a note of special appreciation to my wife Leona, for her patience and encouragement during my graduate career, and for her tireless efforts in typing this manuscript, as well as, her aid in preparing some of the figures.