FERROMAGNETISM AND ORDER IN NICKEL MANGANESE ALLOYS

by

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SYNOPSIS

An investigation of ferromagnetism in nickel manganese alloys up to forty atomic percent manganese has been carried out. Twenty alloys within this composition range were subjected to three heat treatments such that the conditions within the alloys varied from atomic disorder to a high degree of long range order.

The degree of order of Ni_3Mn calculated from measured saturation magnetisation using the Ising model of ferromagnetism was consistent with the value calculated from the ratio of measured integrated intensity of the (110) x-ray diffraction superlattice line to that of line (111).

The relationship between saturation magnetisation and concentration for the disordered alloys can be explained adequately by the existence of short range order. A value of 3.4 Bohr magnetons was obtained for the effective magnetic moment of manganese atoms in a nickel lattice.

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FERROMAGNETISM AND ORDER IN NICKEL MANGANESE ALLOYS

Introduction

A ferromagnetic material is defined as a material that has a large force exerted on it when placed in a magnetic field gradient. The source of the ferromagnetism is thought to be the spin of the electrons. Although the orbital motion of the electrons may also have a magnetic moment, this is thought to be small compared with the spin magnetic moment in a solid, as the gyromagnetic ratio is nearly equal to that of an electron spin. For a substance to be magnetic, it is necessary to have more of the electron spin moments oriented in one direction than in the other. If equal numbers of electrons have their spins aligned in each direction, their magnetic moments will cancel and the material as a whole will not be magnetic. In ferromagnetic materials there is a spontaneous

alignment of the electron spins in the partially filled shells of each atom. Because one energy level can only contain one electron of each spin orientation, the alignment of electron spins will raise some of the electrons into higher kinetic energy states. If a magnetic material does not have a high density of states in the unfilled electron shell, then the aligning of the electrons will require more energy than is available. In the Heisenberg theory¹, the energy that aligns the electrons is a result of the electrostatic exchange interaction between the electrons of the atoms. The outer, valence electrons will not take part in the magnetism because the density of states is not sufficiently high. In the transition metals, however, there is an unfilled 3d shell in the iron group and an unfilled 4f shell in the rare earths. It is found that nickel, cobalt, iron, and gadolinium are the only magnetic elements. Slater², using the Heisenberg theory, attributes the lack of magnetism in other elements of the transition groups to the large radius of their 3d shell compared with their relatively small interatomic distance. Under this condition the 3d shells of adjacent atoms will overlap too much causing a negative exchange interaction.

The relative values for the saturation magnetisation of different elements and alloys are often compared with the number of electrons in the 3d shell. There are five quantized energy levels in the 3d shell, each of which can hold two electrons of opposite spin. If this band is divided into two half bands, each of which can hold five electrons of one spin direction, the maximum magnetisation will occur when one of the bands is completely filled and the other band has the remaining 3d electrons. Because the 3d and 4s bands overlap, it is not necessary to have an integral number of electrons in either band, but the total number of

electrons in the 3d plus 4s bands must be the same as that of the free atoms. Because the experimental value for the saturation magnetisation of nickel is 0.6 Bohr magnetons, there must be 0.6 holes in the 3d shell of nickel. This allows 0.6 valence electrons in the 4s shell. If we assume that the number of 4s electrons is constant for atoms with atomic number near that of nickel, then the magnetisation will decrease with atomic number as shown in Figure 1. The experimental curves are shown as a dotted line in Figure 1. It is seen that alloys of nickel and manganese follow the theoretical curve at high nickel concentrations but leave the curve at manganese concentrations greater than eight atomic percent.

The Ising approximation³, in which only the z component of the 3d spin is used in the Heisenberg exchange energy term, can be used to predict the magnetisation of alloys if the magnetic moment of the individual atoms is known. When using this approximation, it is usually assumed that the exchange interaction which aligns the electron spins is constant for small changes in interatomic distance. This approximation has been used by Neel⁴, Vonsovsky⁵, Bitter⁶, Smoluchowsky⁷, and others, to explain ferromagnetism and antiferromagnetism in ferrites and alloys.

The alloys of manganese and nickel are an interesting example of the Ising approximation. When the manganese atoms are added to the nickel lattice their magnetic moments will lie in the same direction as the nickel atoms if the exchange interaction between the manganese and nickel atoms has a positive sign. Because there are more holes in the 3d shell of manganese than of nickel, one would therefore expect a linear increase in saturation magnetisation with increasing manganese concentration. This was found to be true up to six atomic percent manganese by Kaya and Kussmann⁸. Their results for the values of saturation magnetisation extrapolated to zero degrees Kelvin, are shown in Figure 2. The

Figure 1. A plot of magnetic moment per atom against atomic number. The solid line is the theoretical value; the dotted lines show the experimental measurements. ¹⁸

bending over of the curve at eight atomic percent manganese is attributed by Carr⁹ to the negative exchange interaction of the nearest neighbour manganese atoms causing adjacent manganese atoms to have opposite spin. The perfectly ordered face centered cubic structure would, however, have no nearest neighbour manganese atoms below twenty-five atomic percent manganese. One would therefore expect the completely ordered alloy to have a value of saturation magnetisation on the line tangent to the curve at zero percent manganese. The tangent is shown dotted in Figure 2. The ordered alloy of Kaya and Kussmann at twenty-five atomic percent manganese has a value of saturation magnetisation far below the expected value on the tangent. A preliminary heat treatment on an alloy of this composition made during the present work, showed that the saturation magnetisation of Ni_3Mn was much higher than the value found by Kaya and Kussmann. An investigation of the literature on nickel manganese alloys confirmed this higher value. However, no other measurements of saturation magnetisation have been made on alloys other than the stoichiometric composition. The other investigators used different heat treatments and thus obtained different values for the saturation magnetisation of Ni_3Mn . If the alloy is ordered, superlattice lines should occur on the x-ray diffraction pattern. Because the intensity of the superlattice lines depends on the difference between the atomic scattering factors of nickel and manganese, which is small, the superlattice lines were not seen until monochromatic radiation and an evacuated camera were used recently by Averbach¹⁰. Superlattice lines had previously been seen by neutron diffraction¹¹.

Because it was apparent that the heat treatment for much of the work on these alloys has been inadequate to give maximum ordering, it was decided to make a thorough investigation of the magnetic

Figure 2. Values of saturation magnetisation extrapolated to 0°K plotted against atomic percent manganese.

- results of Kaya and Kussmann.⁸

properties of nickel manganese alloys. It was proposed to make alloys in the range zero to thirty-eight atomic percent manganese, to find the heat treatment that will give maximum magnetisation, to measure the saturation magnetisation, and to find the necessary conditions to explain the change in saturation magnetisation with composition using the Ising approximation. It was also proposed to find the order parameter for alloys near the stoichiometric composition by measuring the intensity of the x-ray superlattice lines. Unfortunately, a paper by Carr⁹, which explained the change of saturation magnetisation with composition for the quenched alloys, was published when the present work was half finished.

Previous Work

The change in saturation magnetisation of nickel manganese alloys has been measured from zero to forty weight percent manganese by Kaya and Kussmann⁸. Their results for the values of saturation magnetisation extrapolated to zero degrees Kelvin are shown in Figure 2. They also measured the Curie temperature at all compositions. These results are shown in Figure 3. After a heat treatment at 430° C for three days, their value of magnetic saturation of composition Ni₃Mn was $4\pi I = 7800$ Gauss, compared with a value of 6400 Gauss for nickel under the same conditions.

The alloy Ni₃Mn has been investigated by several people. Thompson¹² obtained parallel effects for the change of magnetisation and resistivity on both annealed and quenched samples. He measured the magnetic Curie temperature at 460° C, the critical ordering temperature at 520° C, and the maximum saturation magnetisation at $\sigma = 91.5$. This is equivalent to $4\pi I = 9500$ Gauss if the density of Ni₃Mn is taken to be 8.25 grams per

Figure 3. Change of Curie temperature with increasing manganese concentration in nickel manganese alloys.
- results of Kaya and Kussmann.⁸

Figure 4. Lattice parameter of nickel manganese alloys
- results of Valentiner and Becker.¹⁵

cubic centimeter. The saturation magnetisation of Ni_3Mn was measured by Guillard¹³ after a heat treatment of three weeks at 470°C . The value of the extrapolated curve to 0°K was $\sigma = 98.16$ Gauss ($4\pi I = 10200$). The saturation magnetisation of Ni_3Mn , measured by Komar and Volkenstein¹⁴, was 9300 Gauss. The change in lattice parameter of quenched alloys with composition, shown in Figure 4, was measured by Valentiner and Becker.¹⁵ The lattice parameter of ordered Ni_3Mn was $3.59 \text{ \AA}$.¹⁰

Procedure

The alloys were made from the following metals: nickel powder from Fisher Scientific Company with 0.1% Fe and less than 0.1% Co as the main impurities; electrolytic manganese donated by the Electromanganese Corporation with 0.018% S as sulphide and 0.015% H_2 as the main impurities. The alloys were melted under an argon atmosphere because a magnetic manganese nitride forms when manganese alloys are melted under air. The alloys could not be melted under vacuum because manganese is too volatile. To obtain the proper argon atmosphere the vacuum melting and casting unit described in Appendix 1 was designed and built. The oxide surface on the nickel powder was reduced by heating the nickel and manganese in the induction furnace at 600°C for ten minutes under a hydrogen atmosphere. After the oxide had been reduced, the furnace was evacuated to 0.5 microns and argon, which had been purified by passing over magnesium chips and copper turnings at 400°C , was let in to a pressure of one atmosphere. The metal was then melted and the alloy was cast under the argon atmosphere into the cold brass mold. This chill casting produces a high concentration gradient for short distances in the

cored structure, thus decreasing the homogenizing time required to remove detectable heterogeneity. To test the ingot for segregation, samples taken from the top, center, and bottom of a cast ingot were analyzed; typical results were: 22.9, 22.6, and 22.7 weight percent manganese. The ingots were homogenized for five days at 1000° C under a purified argon atmosphere.^x

The saturation magnetisation of the alloys was measured on a Fereday magnetic balance.¹⁶ This instrument is described in Appendix 2. The samples for the magnetic balance were cut and filed to shape from the homogenized ingot. The adjacent piece of the ingot was used for the analysis sample. The magnetic samples were annealed at 420° C for two weeks, then at 400° C for one week.^y The correct annealing treatment was found by annealing alloys of 15.35, 19.92, 23.70, and 32.07 atomic percent manganese at temperatures of 370, 400, 420 and 450° C, and

x. A standard quartz tube furnace with rubber bungs at the end of the tube and a heating element sixteen inches long was used. A rubber gas analysis bag connected to the furnace, kept the pressure slightly above one atmosphere.

y. Some previous investigators have used a slow cooling heat treatment on their alloys. If this is done they must assume the alloy is completely ordered after the heat treatment. By using a constant temperature heat treatment, the degree of order for the alloy can be found from the theoretical curve of order against temperature.

measuring the room temperature saturation magnetisation of each sample after different annealing times. All magnetic balance samples were heat treated in evacuated glass tubes with a piece of pure manganese in the tube to absorb any remaining oxygen or nitrogen. The glass tube was heated before it was sealed to remove any occluded gases. Other samples were annealed at 800° C for two hours in evacuated vycor tubes and were quenched in water.

When Debye-Scherrer powder patterns were taken on the annealed alloys, all alloys above eighteen atomic percent manganese had diffuse back reflection lines. This effect is due to a change in lattice parameter in the sample, which can be produced by any of the following:

1. an oxide layer on the surface of the powder.
2. small order domains resulting in many Mn-Mn interactions between manganese atoms with the same spin direction at the domain interfaces.
3. internal stresses produced during filing.

To check for the possibility of an oxide layer, a powder sample of 23.7 atomic percent manganese was heated at 420° C for sixteen hours. An x-ray pattern was taken showing diffuse lines. The powder was reannealed at 800° C for two hours and quenched. The pattern of the quenched sample had sharp lines. This showed that no oxide layer was present. To check for the possibility of internal stresses still being present, a powder sample of 23.7 atomic percent manganese was annealed at 550° C for sixteen hours and then at 420° C for fourteen hours. The resulting film had sharp back reflection lines. This confirms the presence of residual strain from the filing, in the alloys annealed at 420° C for two weeks plus 400° C for one week. Apparently the recrystallisation temperature of nickel

manganese alloys increases with manganese content because the alloys with less than eighteen percent manganese had sharp back reflection lines with the same heat treatment in which alloys with higher manganese concentration had diffuse lines. This, however, does not eliminate the possibility of small order domains causing the diffuse lines, as the alloy with heat treatment at 550° C for sixteen hours plus fourteen hours at 420° C may not be sufficiently ordered to produce this effect.

It has been shown by Sykes and Jones¹⁷ that the order domain size is increased by annealing just below the critical order temperature. A preliminary heat treatment was given samples of 23.7 atomic percent manganese to determine the length of annealing time at 490° C that is necessary to produce large order domains. Samples of the alloy were annealed at 490° C for different times, and were then annealed at 420° C for two weeks. It was found that the saturation magnetisation of the alloy increased with the time of annealing at 490° C up to a period of 200 hours. For the final heat treatment, alloys of composition 19.9, 21.8, 23.7, 24.1, 25.0, 25.7, 27.9, and 30.3 atomic percent manganese were annealed at 555° C for fourteen hours, plus 250 hours at 490° C, plus 260 hours at 420° C, plus 260 hours at 400° C. Powder patterns were taken of these alloys and their saturation magnetisation was measured.

The intensity of the (110) superlattice line on the alloy of twenty-five atomic percent manganese was measured on the Philips goniometer by taking the total count for an hour with the geiger counter oscillating across the line. The background was taken under the same conditions on both sides of the line. The intensity of the (111) line was then measured in a similar manner.

Results

In the first set of preliminary samples for the magnetic balance, a heavy oxide formed when the samples were annealed in 'evacuated' pyrex tubes that were incorrectly sealed. The curve of magnetisation against annealing time for these samples followed the curve later found for magnetisation against decreasing manganese content. The oxide was obviously reducing the manganese concentration of the samples. To prevent this oxide from forming, pieces of pure manganese were put in the evacuated tubes with the magnetic balance samples. After being sealed, the pure manganese was slid to one end of the tube and the tube was heated at the manganese end with a gas flame. It was hoped that the hot manganese would absorb any of the remaining oxygen and nitrogen. It was found after several trials, that the local heating of the manganese introduced more gas into the tube from the softened glass than was absorbed by the manganese. The local heat treatment was therefore stopped and all samples on the final runs were annealed in evacuated tubes with a piece of manganese and were not contaminated. Several other investigators have noticed a decrease in manganese content on annealing for a few hours and attributed it to the sublimation of the manganese atoms. This effect is reduced by putting in the pure manganese. To check for any gain or loss in manganese concentration during the heat treatment, the sample for the magnetic balance with 23.7 atomic percent manganese was analyzed at 24.0 atomic percent manganese after annealing for two weeks at 420° C and one week at 400° C.

The following results were obtained from the preliminary runs:

1. The saturation magnetisation of the alloy with 15.4 atomic percent manganese was unchanged by annealing at 380, 400, 420, or 450° C.
2. The curves of saturation magnetisation against annealing time at 380, 400, 420, and 450° C for an alloy with 23.7 atomic percent manganese are shown in Figure 5. The curves for the other alloys are similar.
3. In the course of the magnetic measurements for the preliminary runs, the magnetisation of the standard nickel sample was measured twenty times on different days. It gave a room temperature value of 6000 with a standard deviation of 60.
4. The x-ray diffraction pattern of the 23.7 atomic percent manganese alloy annealed at 420° C for sixteen hours is shown in Figure 6, film A. The pattern for this same alloy after an additional anneal at 800° C with a water quench, is shown in Figure 6, Film B.
5. The saturation magnetisation of samples with 23.7 atomic percent manganese annealed for varying times at 490° C plus an additional two weeks at 420° C is shown in Figure 7.

For the results of the final runs, the following notation is used for the heat treatments:

Heat treatment A - Two hours at 800° C followed by a water quench.

Heat treatment B - Two weeks at 420° C plus one week at 400°C.

Heat treatment C - Sixteen hours at 555°C, plus 250 hours at 490°C,
plus 260 hours at 420°C, plus 260 hours at 400°C.

The following results were obtained from the final runs:

1. The values of the saturation magnetisation for heat treatment A measured at room, dry ice, and liquid oxygen temperatures are shown in Table 1. The value of saturation magnetisation after extrapolation of the magnetisation against T^2 curve to zero degrees Kelvin is also given for

the samples in which the curve was linear.

2. The values of saturation magnetisation for heat treatment B are shown in Table 1. The extrapolated values of saturation magnetisation for heat treatments A, B and C are shown in Figure 8.

3. Figure 9, films A, B, and C show the x-ray diffraction patterns obtained for alloys with 23.7 atomic percent manganese after heat treatment A, B, and C respectively.

4. The values of saturation magnetisation for the samples after heat treatment C are shown in Table 1. The results of the extrapolated curve to zero degrees Kelvin are shown in Figure 10. The corresponding curve for heat treatment B is drawn on the same graph.

5. The x-ray diffraction patterns of alloys with 23.7, 25.0, and 25.7 atomic percent manganese after heat treatment C are shown in Figure 11, films A, B, and C. The prints were over-exposed to bring out the order lines. This is the reason why the doublets are not resolved.

6. The results for the line intensity measurements are given below:

Line	<u>oscillating angle</u>		Time	Counts	Total oscillating angle(2 θ)
	min.	max.			
background (110)	42.96	44.02	1 hour	72450	
(110)	44.28	45.49	1 hour	74314	1.21°
background (110)	45.61	46.58	1 hour	72889	
background (111)	53.95	54.92	20 min.	26584	
(111)	54.83	56.36	20 min.	85387	1.53°
background (111)	56.71	57.70	20 min.	28079

Figure 5. Change in saturation magnetisation for an alloy of 23.7% Mn with increasing annealing time. All measurements were done at room temperature.

Figure 6. Film A - 23.7% Mn after 16 hours at 420°C.

- unfiltered Cu radiation

Film B - same sample as film A with an additional

2 hours at 800°C followed by a water quench.

- unfiltered Cu radiation.

Figure 7. Room temperature values of saturation magnetisation for samples of 23.7% Mn annealed for varying times at 490°C with an additional 400 hours at 420°C.

Saturation Magnetisation $4\pi I$ in Gauss												
%Mn	Heat Treatment A				Heat Treatment B				Heat Treatment C			
	293°K	200°K	90°K	0°K	293°K	200°K	90°K	0°K	293°K	200°K	90°K	0°K
0					6203	6400	6400	6400				
3.9	6880	7250	7690	7810	6940	7340	7530	7600				
4.8	6940	7440	7730	7810	6960	7510	7750	7800				
6.4	7120	7700	8100	8200	7190	7810	8240	8330				
7.4	7060	7740	8130	8210	7320	7980	8380	8480				
11.1	6680	7610	8410	8550	6700	7730	8290	8470				
12.7	5860	7070	7800	8000	6050	7180	7990	8170				
15.4	4740	6210	7020	7220	5470	6830	7660	7850				
16.0	4270	5900	6647	6890	4720	6230	7090	7340				
18.3	1984	4460	5520	5820	4250	5840	6702	6870				
19.9	740	3670	4850	5140	3860	5450	6210	6350	3750	5360	6186	6540
21.8	100	1030	2780		8540	9050	9270	9320	7630	8300	8540	8590
23.7	100	370	1450		9440	9500	9450	9480	9890	9880	9850	9880
24.1	60	180	890		9370	9340	9330	9350	10730	11010	10910	11000
25.0	50	110	400		7830	8240	8350	8380	10130	10260	10340	10350
25.7	40	100	300						9510	9750	9910	10020
28.0	50	70	130		7360	7710	7800	7820	7070	7950	7840	7900
30.3	32	50	64	71	6850	7160	7270	7310	6710	6890	7010	7070
32.1	32	46	28	0	590	640	620	620				
37.0	14	0	4	0	340	320	330	330				

Table 1. The above values were obtained relative to the standard nickel sample, with a correction for the change in weight of the average atom and the change in lattice parameter as shown in Figure 4.

Figure 8. Values of saturation magnetisation extrapolated to zero degrees Kelvin for heat treatments A, B, and C.

Figure 9. X-ray diffraction patterns for an alloy with 23.7 atomic percent manganese after heat treatment A, B, and C are shown in films A, B, and C respectively. Unfiltered iron radiation was used.

Figure 10. Values of saturation magnetisation extrapolated to zero degrees Kelvin for heat treatments B and C.

Figure 11. X-ray diffraction patterns for alloys with 23.7, 25.0, and 25.7 atomic percent manganese after heat treatment C are shown in films A, B, and C respectively. Unfiltered iron radiation was used.

Discussion

1. Preliminary Runs.

From Figure 5 showing the change of magnetisation with annealing time at 420°C, it is evident that saturation magnetisation increases progressively with annealing time for periods up to two weeks. Most other investigators have only used times in the order of fifty hours. The value of the saturation magnetisation after annealing at 420°C is influenced by the length of the previous anneal at 490°C. This change, shown in Figure 7, is due to the size of the order domains increasing at the high temperature anneal.

2. Final Runs.

a. Disordered case after heat treatment A.

The tail above twenty-five atomic percent manganese in the curve of saturation magnetisation against concentration for the quenched alloys is probably due to the slow quenching rate, as the vycor tubes were not broken when they were quenched into the water. The curve of Kaya and Kussmann, shown in Figure 2, has no tail.

It was noticed that the curve of magnetisation against T^2 was not linear for the quenched samples between twenty and thirty atomic percent manganese. These alloys had much too low a value of saturation magnetisation at 200°K to fit the T^2 curve. This effect is also present in the work of Kaya and Kussmann⁸. It is probably due to the magnetic field strength not being sufficient to saturate the samples. If the samples had a coercive force that was small at 90°K and 293°K, and was large at 200°K, then it would be possible for the magnetic field to saturate the samples

at 90°K and 293°K but not be strong enough to saturate them at 200°K. The only alloys that have non linear curves are the quenched alloys near the order composition. If local order exists, then these alloys will have an order domain size that is larger than the domain size of the other quenched alloys and smaller than the domain size of the annealed alloys near the order composition. It is a known fact that the magnetic coercive force reaches a maximum at one magnetic domain size and is smaller for either larger or smaller domains. Because the maximum size of the magnetic domains is less than the size of the order domains, the non linear curves for the quenched alloys can be explained by assuming that the order domains of these alloys are the proper size to produce the critical magnetic domain size for maximum coercive force.

Carr⁹, in a recent paper, qualitatively explains the behaviour of the saturation magnetisation of the quenched alloys in terms of the number of Mn-Mn interactions. He proposes the following theory:

'For a disordered alloy with an appreciable percentage of manganese atoms, the Mn-Mn interaction begins to outweigh the weaker Ni-Mn interaction, and one eventually finds the manganese spins start to cancel one another. This behaviour becomes clearer in the energy calculations which follow and which indicate that the bending over of the curve as observed in Figure 2, should occur for a relatively small fraction of manganese. Beyond this point, the magnetic moment is derived principally from the nickel ions and diminishes with increasing manganese content because of the replacement of nickel and to the filling up of the nickel 3d shell. Assuming the manganese ions to have five electrons in the 3d shell, one finds that the nickel shells become completely filled at about 30 percent manganese. The

moment thus goes to zero at this composition in approximate agreement with experiment.'

If we assume that for low manganese concentrations there are no Mn-Mn interactions, then from the initial slope of the curve in Figure 8, we find that the addition of manganese atoms to a nickel lattice produces a rise in magnetisation similar to that produced by an atom with a magnetic moment in the order of 3.4 Bohr magnetons. Other values for the magnetic moment of manganese are:¹⁸

MnAs - 3.40	Mn ₂ Sb - 0.94
MnBi - 3.52	MnSb - 3.53
Mn ₄ N - 0.24	Mn ₂ Sn - 0.86
MnP - 1.2	

The value obtained in this alloy is 5.7 times the magnetic moment of a nickel atom. If we use the Zener assumption¹⁹ that the manganese atoms will retain five of their 3d electrons and the rest will be given to the nickel, then each manganese atom will give $10-5-3.4 = 1.6$ electrons to the nickel atoms. This will make the magnetic moment of the nickel atoms equal zero at twenty-seven atomic percent manganese.

Carr⁹ assumes that the magnetisation near twenty-five atomic percent manganese is due to the nickel atoms alone. If this is true, then the curve near twenty-five atomic percent manganese will have a slope equal to $-\frac{6400}{25} = -256$ using the units on Figure 8. The actual slope is -960. This discrepancy can be eliminated by having the manganese atoms contribute to the magnetism up to twenty-five atomic percent manganese and above this concentration having all the manganese atoms paired off. It can be accomplished in either of two ways:

1. by assuming that the strength of the Mn-Mn interaction is such that

it finally overpowers the Mn-Ni interaction at twenty-five atomic percent manganese.

2. by assuming that local order exists that tends to keep the manganese atoms from becoming nearest neighbours in the quenched alloys. The degree of order is such that below twenty-five atomic percent manganese there are insufficient Mn-Mn interactions to make the contribution of the manganese atoms to the magnetic moment of the alloy equal to zero.

Of these two assumptions, the latter is preferable for the following reasons:

a. It is shown in Appendix four, that when the first assumption is used, the value obtained for the final slope of the curve near twenty-five atomic percent manganese is only half the experimental value.

b. The Mn-Mn interaction should outweigh the Ni-Mn interaction at a manganese concentration lower than twenty-five atomic percent because the strength of the Mn-Ni interaction becomes weaker as the 3d shells of the nickel atoms become filled.

c. In a previous section of the discussion, it was shown that the non-linearity of the saturation magnetisation against T^2 curve for some of the quenched alloys can be explained by assuming short range order.

d. Some degree of short range order is present in all alloys.²⁰

Examples of this are the local order in AgAu for which there is no long range order, and the local order in quenched samples of Cu₃Au.

e. The saturation magnetisation is the same for quenched and annealed alloys up to nine atomic percent manganese. The Curie temperature is the same for quenched and annealed alloys up to seventeen atomic percent manganese. Because the annealed alloys will be ordered, then so will the quenched alloys if their magnetisation and Curie temperatures are the same.

2b. Ordered Alloys.

The maximum in saturation magnetisation for the ordered alloys occurs at a concentration less than twenty-five atomic percent manganese because the alloy is not completely ordered. An incompletely ordered alloy at twenty-five atomic percent must have some of its manganese atoms with left spin, but an incompletely ordered alloy at less than twenty-five atomic percent manganese may accomplish its disorder by having nickel atoms in manganese sites and therefore does not need to have any manganese atoms with left spin. It is seen from figures 8 and 10, that heat treatment C produces a maximum in the graph of saturation magnetisation versus composition at 24.1 atomic percent manganese and heat treatment B, which produces less long range order than heat treatment C, results in a maximum in saturation magnetisation at 23.7 atomic percent manganese.

The drop in magnetisation of Ni_3Mn from the ordered value of 13400 to the value of 8380 after heat treatment B, can be explained by assuming that the magnetic moment of a manganese atom with reversed spin, will cancel the magnetic moment of one manganese atom with right spin. To account for the magnetic moment found experimentally in heat treatment B using the above assumption, we must have 0.187 of the manganese atoms with left spin. Therefore these atoms must occupy face centered positions. Using this value we get $S = 0.81$ from the Bragg and Williams theory and $\sigma = 0.63$ from equations 14 of Appendix 3, using the local order theory, if we assume that each manganese atom with left spin produces three Mn-Mn interactions. The calculations are shown in Appendix 5. The short range order parameter of heat treatment B gives a value of $S = 0.77$ for the long range order parameter. Similar values for heat

treatment C were: $S = 0.89$ for the Bragg and Williams, and $\sigma = 0.77$ for the short range order theory which makes $S = 0.88$ for this theory. References 21 and 22 give the following equilibrium values of S at 400°C with a critical order temperature of 520°C :

Bragg and Williams theory $S = 0.79$

Bethe and Peierls theory $S = 0.95$

Cu_3Au experimental $S = 0.98$

The low value of S obtained from the results of heat treatment B may be partially due to the small order domain size. Neither of the theories includes a factor for the domain size. Another possible reason for the low value of S , is the assumption that a manganese atom in a face centered position reverses its spin and does not influence the spin of its nearest neighbour manganese atoms. If the reversed spin of one manganese atom reduced the effective spin of its three adjacent manganese atoms, then a small amount of disorder would produce a larger decrease in the magnetisation than that calculated. This would raise the value of the order parameter calculated from the experimental results of saturation magnetisation.

The values of saturation magnetisation for the annealed alloys above thirty and below twenty-one atomic percent manganese are not as high as those expected, because long range order is not present and thus there are more Mn-Mn interactions than if it were present.

The Curie temperature of a magnetic material is directly proportional to the strengths of the interactions between the magnetic moments of the atoms of the material. From the decrease in Curie temperature with the addition of manganese atoms in the nickel lattice, shown in Figure 3, it is concluded that the Mn-Ni interaction is much smaller

than the Ni-Ni interaction at this composition. The high Curie temperatures of the ordered alloy is probably due to the second nearest neighbour interaction between the manganese atoms on the cube corners. This would account for the rapid rise in Curie temperature near twenty atomic percent manganese when long distance order is increasing rapidly. It also accounts for the maintaining of the high Curie temperature for compositions greater than twenty-five atomic percent manganese because there are still the same number of second neighbour Mn-Mn interactions that are present in the alloy with twenty-five atomic percent manganese.

The value of the order parameter of the alloy with twenty-five atomic percent manganese after heat treatment C was calculated from the measured intensity of the (110) planes compared with the (111) planes. The calculations are shown in Appendix 5. The value obtained was $S = 0.84 \pm 0.07$. The order parameter for the same alloy calculated from the saturation magnetisation was $S = 0.88$. This agreement is fairly good and justifies the assumption that the Mn atoms in the face centered position invert their spins and thus cancel the magnetic moment of one of the manganese atoms at the cube corner.

Probably the weakest point in the explanation of the change in saturation magnetisation with concentration is the assumption that the 3d shells of the nickel atoms are being filled with increasing manganese content. This principle is in accord with Zener's theory¹⁹ but does not necessarily occur in all alloys, as evidenced by neutron diffraction experiments on FeCo. If we do not assume that the 3d shells of the nickel atoms are filled, then there is no explanation for the decrease in saturation magnetisation to zero at twenty-five atomic percent manganese for the quenched alloys. Unfortunately, there is no way to test this

assumption for the quenched alloys. In the case of the ordered alloys it could be checked by an evaluation of the magnetic moments of the manganese and nickel atoms by neutron diffraction on a completely ordered alloy.

Conclusions

The annealing times used by most other investigators to produce complete order in alloys near the composition Ni_3Mn have been inadequate. To produce the equilibrium degree of order at 420°C , at least two weeks annealing time is necessary.

The maximum value for the saturation magnetisation of any alloy of nickel and manganese less than forty percent manganese, after heat treatment C, is $4\pi I = 10980$ Gauss. This is the highest recorded value for any nickel manganese alloy after any heat treatment.

The order domain size in Ni_3Mn increases with annealing time at 490°C up to periods of 200 hours. When this annealing treatment is followed by an additional 250 hours at 420°C , and 250 hours at 400°C , the order lines can be seen on an x-ray powder pattern using iron radiation. For these long heat treatments, it is necessary to have a piece of pure manganese with the sample to prevent the sublimation of the manganese atoms from the sample.

The order parameter of Ni_3Mn after the heat treatment given in the paragraph above is $S = 0.88$, calculated from the saturation magnetisation, and $S = 0.84 \pm 0.07$, calculated from the order line intensity.

The addition of manganese atoms to a nickel lattice produces a rise in saturation magnetisation that is similar to that produced

by an atom with a magnetic moment of 3.4 Bohr magnetons.

To explain the change in saturation magnetisation of alloys quenched from 800°C, it is necessary to assume that some of the 3d electrons from the manganese atoms go into the 3d shell of the nickel atoms. Once this assumption has been made, the curve of saturation magnetisation against composition for the quenched alloys can be explained most satisfactorily by the existence of short range order.

APPENDIX 1

Vacuum Melting and Casting Apparatus

To prevent the contamination of the metals by nitrogen and oxygen, a high frequency vacuum melting apparatus was designed and built. The apparatus consisted of two parts; a general vacuum pumping unit shown in Figure 12, and a high frequency induction furnace shown in Figure 13. Photographs of the complete unit are shown in Figures 14 and 15.

The brass pumping unit consisted of a Welsh duoseal fore-pump with a pumping speed of 0.37 liters per second at 0.1 millimeters pressure, a VMF 50 oil diffusion pump, a cold trap, a Kinney vacuum valve, a pirani gauge, and an ionization gauge. A three inch brass tee was connected to the end of the unit. All parts of the unit were connected with eight-bolt companion flanges using greased rubber gaskets. The gasket groove had a beveled edge to prevent the gasket from being pinched when the bolts were tightened. For argon melting, a bourdon gauge was connected to the pumping unit. This was necessary to measure the pressure when the argon was let into the system.

The high frequency induction furnace was attached to the brass tee of the pumping unit with a companion flange. The quartz tube (fourteen inches long and one and one half inches in diameter) was connected to the brass by using a mixture of graphite, octoil, and digested rubber in vacuum wax. This mixture had physical properties similar to plasticene except that its vapour pressure was lower. The seal at the top end of the furnace was water cooled. The power was supplied by a Lepel

7.5 KVA high frequency unit. The water cooled high frequency coil had sixteen turns in four inches length. The crucibles were Norton extraction thimbles made of alundum, with powdered alundum packed between them. The inner crucible, which could be used for several melts, held fifty grams of powdered nickel. The loaded crucible was inserted into the top of the quartz tube when the mold was removed. The crucible was then lowered into the middle of the high frequency coil by lowering the rod through the vacuum compression seal at the bottom of the furnace. The mold was replaced at the top of the furnace and the forepump started. It took approximately seven minutes pumping time to reduce the pressure to 0.1 millimeters, which is the forepressure of the oil diffusion pump. The total pumping time to reach 0.5 microns pressure was from thirty to forty minutes. After the metal was melted in the crucible, the rod at the bottom of the furnace was pushed up, thus lifting the crucible containing the molten metal to the height of the brass mold. The whole furnace was then rotated through one hundred degrees about the O-ring seal and the metal flowed into the cold mold.

Figure 12. Diagrammatic view of the vacuum pumping system.

figure 13. Diagrammatic view of the high frequency
induction furnace and vacuum casting unit.

Figure 14. Photograph of vacuum melting and casting unit
- front view.

Figure 15. Photograph of vacuum melting and casting unit
- rear view.

APPENDIX 2

Magnetic Balance

1. Description.

The saturation magnetisation of the alloys was measured on a magnetic balance similar to that of Fereday¹⁶. The electromagnet had 7000 turns and produced a field of 3000 Oersteds. The special magnet poles designed by Fereday produced a magnetic field such that the force on a sample was constant along the pole axis near the center of the gap. The samples were $\frac{1}{4} \times \frac{1}{20} \times \frac{1}{20}$ inches. The sample holder was attached to the end of the suspension arm shown in Figure 16. When the current was on in the electromagnet, the sample was displaced toward one of the poles. It was then restored to its initial position by twisting the suspension. The angle through which the suspension was twisted was controlled and measured by a worm gear at the top of the suspension. The initial position of the arm could be found by shining a light to the mirror on the suspension and back to a scale. The angle through which the suspension was turned was directly proportional to the force on the sample caused by the magnetic field gradient. The saturation magnetisation for a sample was found by comparing the force on it to the force on a standard nickel sample. To measure the saturation magnetisation at high and low temperatures, the furnace shown in Figure 17 and the dewar flask shown in Figure 18 were used.

Figure 16. Front view of magnetic balance showing magnet, suspension and sample holder.

Figure 17. Top view of magnetic balance showing worm gear control and furnace arrangement.

Figure 18. Top view of magnetic balance showing dewar flask arrangement.

2. Calibration.

a. Plotting of magnetic field in the air gap.

The relative change of the magnetic field in the air gap was investigated using the analogy between magnetostatic and electrostatic fields. Because the magnetic field between the pole pieces is constant with time, the magnetic potential satisfies Laplace's equation. Therefore, if the boundary conditions for the magnetic and electric fields are the same, the potentials will be relatively the same over all points in the field. Using this principle, relative values of the magnetic field in the air gap of the magnetic balance were found by measuring electrostatic potentials. To obtain similar boundary conditions, the pole pieces of the magnet were removed and placed the same distance apart in a tank of water. An electric potential was put on one of the pole pieces and the other pole was grounded; the potential was then measured at all points on a horizontal plane through the center of the pole pieces.

The vertical probe was made from a piece of insulated wire with a tip bare. To ensure that the insulated section of the probe did not distort the field, readings were taken on a line along the axis of the probe, perpendicular to the axis of the magnet poles and midway between them. If the insulated part of the probe was distorting the field, the readings for which the probe point was below the pole axis would not be the same as the readings above the pole axis. Figure 19, a plot of these readings, shows that the insulated wire does not distort the field. Figure 21 gives a plot of the potentials for the positions in the field shown in Figure 20. The potential along the pole axis is shown in Figure 22. The results of this investigation were:

1. The field was constant over the cross-section of the sample perpendicular to the pole axis.

2. The force on the sample, which is proportional to $\text{grad } H$, was constant for a distance of approximately one half inch along the field axis in the center of the gap. The choice of rest point for the suspension is therefore not critical.

b. Calibration for a change in sample weight.

The Alnico nickel samples used for this calibration were of two different shapes. One shape was cylindrical with the ratio of length to diameter equal to five. The other shape was the same except it had a square cross-section instead of a circle. The ratio of width to length was the same for all samples. The results are shown in Figure 23. The circles are values for samples with a round cross-section; the dots are for samples with a square cross-section. It was therefore shown that the deflection on the magnetic balance divided by the weight of the sample was constant. The constant was the same for both shapes and all weights of the samples investigated.

Figure 19. Test of probe used in measurement of the electrostatic potentials between the magnet poles.

Figure 20. Position in air gap between the magnet poles for the potential measurements shown in Figure 21.

Figure 21. Potential at various points in the air gap between the magnet poles. The position of the readings is shown in Figure 20.

Figure 22. Potentials along the magnet pole axis.

Figure 23. Calibration of magnetic balance for sample weight.

The dots are measurements on samples with square cross-section; the circles on samples with round cross-section.

APPENDIX THREE

Statistical Derivations

1. Definitions.

Let the face centered cubic lattice be divided into four simple cubic lattices L_1 , L_2 , L_3 , and L_4 , such that an atom in one sublattice has four nearest neighbours in each of the other three sublattices but no nearest neighbours in its own sublattice.

Let the order parameters of L_1 , L_2 , L_3 , and L_4 be a , b , c , and d , respectively. If f_{1A} is the fraction of L_1 sites occupied by A atoms

$$\text{Let } a = 2f_{1A} - 1 \quad 1$$

when $a = 1$ all atoms on L_1 are A atoms

when $a = 0$ one half the atoms on L_1 are A atoms

when $a = -1$ no atoms on L_1 are A atoms

similarly: $b = 2f_{2A} - 1$

$$c = 2f_{3A} - 1$$

$$d = 2f_{4A} - 1$$

We therefore get the equations

$$f_{1A} = \frac{1+a}{2} \quad f_{1B} = 1 - f_{1A} = \frac{1-a}{2}$$

with similar equations for the other sublattices.

$$\text{Let } (a + b + c + d) = R \quad 2$$

Let F_A be the total fraction of A atoms in the alloy.

$$F_A = \frac{f_{1A} + f_{2A} + f_{3A} + f_{4A}}{4}$$

$$= 1/2 + 1/8 (a + b + c + d)$$

$$F_A = 1/2 + 1/8 R \quad 3$$

$$F_B = 1/2 - 1/8 R \quad 4$$

Let z be the coordination number of the lattice.

2. Derivation of Equations.

Consider the nearest neighbour interactions of the atoms in sublattice L_1 with the atoms in L_2 , L_3 , and L_4 . The total number of A atoms and B atoms in L_1 is $\left(\frac{1+a}{2}\right) \frac{N}{4}$ and $\left(\frac{1-a}{2}\right) \frac{N}{4}$ respectively. The probability of any one atom in lattice L_1 being an A atom, is equal to the fraction of A atoms in L_1 .

Using these last three facts, the number of A-A interactions where one of the A atoms is in L_1 is:

$$\left(\frac{1+a}{2}\right) \frac{N}{4} \left[\frac{z}{3} \left(\frac{1+b}{2}\right) + \frac{z}{3} \left(\frac{1+c}{2}\right) + \frac{z}{3} \left(\frac{1+d}{2}\right) \right]$$

which equals $\frac{Nz}{48} [3 + 2a + R + ab + ac + ad] \quad 5$

Similarly, the number of B-B interactions, where one of the B atoms is in L_1 is:

$$\left(\frac{1-a}{2}\right) \frac{N}{4} \left[\frac{z}{3} \left(\frac{1-b}{2}\right) + \frac{z}{3} \left(\frac{1-c}{2}\right) + \frac{z}{3} \left(\frac{1-d}{2}\right) \right] \quad 6$$

which equals

$$\frac{Nz}{48} [3 - 2a - R + ab + ac + ad]$$

The number of A - B interactions in which the A atom is in L_1 is:

$$\frac{Nz}{48} [3 + 4a - R - (ab + ac + ad)]$$

The number of B - A interactions in which the B atom is in L_1 is:

$$\frac{Nz}{48} \left[3 - 4a + R - (ab + ac + ad) \right]$$

Since A-B interactions are equivalent to B-A interactions, the sum of the last two equations will be the number of A-B interactions in which one of the atoms is on L_1 . This equals

$$\frac{Nz}{48} \left[6 - 2(ab + ac + ad) \right] \quad \dots \dots \dots 7$$

Equations similar to 5, 6, and 7 are derived using L_2 , L_3 , and L_4 in turn as the reference axis. The total number of A-A interactions is the sum of equation 5 with the three similar equations obtained by considering the A-A interactions using L_2 , L_3 , and L_4 as the reference lattice, all divided by 2.

Let Q_{AA} , Q_{BB} and Q_{AB} be the total number of A-A, B-B, and A-B interactions, respectively.

$$Q_{AA} = \frac{Nz}{96} \left[12 + 6R + 2(ab + ac + ad + bc + bd + cd) \right]$$

but $z = 12$ for the fcc lattice.

$$Q_{AA} = \frac{N}{8} \left[12 + 6R + R^2 - (a^2 + b^2 + c^2 + d^2) \right] \quad \dots \dots \dots 8$$

similarly

$$Q_{BB} = \frac{N}{8} \left[12 - 6R + R^2 - (a^2 + b^2 + c^2 + d^2) \right] \quad \dots \dots \dots 9$$

$$Q_{AB} = \frac{N}{8} \left[24 - 2R^2 + 2(a^2 + b^2 + c^2 + d^2) \right] \quad \dots \dots \dots 10$$

It is seen that the total number of interactions obtained by adding equation 8, 9 and 10 is $6N$. This is in agreement with the coordination number of twelve.

Case 1. Disordered lattice.

When the lattice is completely disordered,

$$a = b = c = d = 2f_{1A} - 1 = 2F_A - 1$$

$$R = a + b + c + d = 4a = 4(2F_A - 1)$$

Putting these values of a , b , c , d , and R into equations 8, 9 and 10 we get

$$(Q_{AA})_{\text{dis}} = 6 F_A^2 N \quad \dots \dots \dots 11$$

$$(Q_{BB})_{\text{dis}} = 6 N [F_A^2 - 2F_A + 1] \quad \dots \dots \dots 12$$

$$(Q_{AB})_{\text{dis}} = 12 N (F_A - F_A^2) \quad \dots \dots \dots 13$$

Case II. Ordered Lattice.

Let L_1 be the sublattice containing the B atoms when fully ordered.

Assume: (1) that all B atoms lie in the one sublattice L_1 (it is immaterial which sublattice they are in as long as they all lie in the same one)

(2) the other three sublattices are indistinguishable, i.e.,

$$b = c = d$$

$$\text{Case IIa.} \quad F_A \geq \frac{3}{4}$$

then $b = c = d = 1$ as these lattices have no B atoms

$$\text{but } a + b + c + d = R = 4(2F_A - 1)$$

$$a = 8F_A - 7$$

putting these values of a , b , c , d into equations 8, 9, 10, we get

$$\left. \begin{aligned} (Q_{AA})_{\text{ord}} &= (96 F_A - 48) \frac{N}{8} = N (12F_A - 6) \\ (Q_{BB})_{\text{ord}} &= 0 \\ (Q_{AB})_{\text{ord}} &= (-96F_A + 96) \frac{N}{8} = 12N (1 - F_A) \end{aligned} \right] \quad \left. \begin{aligned} &F_A \geq \frac{3}{4} \\ &\dots \dots \dots 14 \end{aligned} \right]$$

Case IIb.

$$F_A \leq \frac{3}{4}$$

Assume L_1 lattice is filled with B atoms, i.e. $a = -1$

Let $b = c = d$

$$\text{but } a + b + c + d = R = 4 (2F_A - 1)$$

$$b = \frac{8}{3} F_A - 1$$

putting these values into equations 8, 9, 10 we get

$$\left. \begin{aligned} (Q_{AA})_{\text{ord}} &= \frac{16N}{3} F_A^2 \\ (Q_{BB})_{\text{ord}} &= \frac{16}{3} F_A^2 - 12F_A + 6 N \\ (Q_{AB})_{\text{ord}} &= 12F_A - \frac{32}{3} F_A^2 N \end{aligned} \right\}$$

$$F_A \leq \frac{3}{4} \dots\dots\dots 15$$

these check with case IIa for $F_A = \frac{3}{4}$

APPENDIX 4

Equations for the Quenched Alloys

The object of this Appendix is to find the slope of the curve of saturation magnetisation of the quenched alloys near twenty-five atomic percent manganese assuming the alloys are disordered.

Near twenty-five atomic percent manganese the 3d shell of the nickel will be nearly filled. One would therefore expect the Mn-Mn interaction to be much stronger than the Mn-Ni interaction, which in turn will be much stronger than the Ni-Ni interaction. Therefore the fraction of manganese atoms with left spin should be proportional to Q_{BB} , the number of Mn-Mn interactions. Because the Mn-Ni interaction is much stronger than the Ni-Ni interaction, one would also expect the spin of a nickel atom to be in the same direction as the spin of its adjacent manganese atom. This is equivalent to saying the fraction of nickel atoms with left spin is the same as the fraction of manganese atoms with left spin.

If we assume the number of manganese atoms with left spin is KQ_{BB} , then the fraction with left spin is $\frac{KQ_{BB}}{F_B N}$. When the value of Q_{BB} for the disordered alloy is substituted from equation 12, Appendix 3, the fraction of manganese atoms with left spin is $6KF_B$. For the manganese contribution to the magnetic moment to equal zero at twenty-five atomic percent manganese, $6KF_B$ must equal $1/2$ at F_B equal to $1/4$. Therefore $K = \frac{1}{3}$. Therefore the fraction of manganese and nickel atoms with left spin is $2F_B$.

If the 3d electrons of the manganese go into the nickel 3d shell, then the magnetic moment of a manganese atom is five Bohr magnetons, and that of a nickel atom is $\mu_{\text{Ni}} = 0.6 - \frac{0.6}{.26} F_B$. When the ordinate is changed to make $\mu_{\text{Ni}} = 1 - 3.8 F_B$, then $\mu_{\text{Mn}} = 8.3$.

Therefore the manganese contribution to the magnetic moment of the metal is $8.3 F_B N(1 - 4F_B)$ and the nickel contribution to the magnetic moment is $F_B N(1 - 3.8F_B)(1 - 4F_B)$. The total magnetic moment is the sum of these and equals:

$$M_T = [8.3F_B + (1 - F_B)(1 - 3.8F_B)] [1 - 4F_B]N$$

$$\left(\frac{dM_T}{dF_B} \right)_{F_B} = \frac{1}{4} = -8.4$$

The experimental curve in the same units has a slope of -15.00. Therefore, the theoretical curve for the saturation magnetisation near twenty-five atomic percent manganese using these assumptions has a slope of approximately one half the experimental value.

APPENDIX FIVE

Calculations of Order Parameters

1. Calculation of the order parameter of Ni_3Mn after heat treatments B and C.

If we assume that all manganese atoms in face centered sites will reverse their spin without affecting the spins of the adjacent manganese atoms, and that the number of nickel atoms with reversed spins is equal to the number of manganese atoms with reversed spins, then the observed drop in magnetisation from 14700 on the tangent to 9500 for the experimental value of heat treatment B can be explained by saying that the fraction of manganese atoms in face centered sites is $\frac{1}{2} \left[\frac{13400-8380}{13400} \right] = .187$

When any lattice site is chosen at random, the probability for it to have the right atom is r , and the wrong atom is w . The Bragg and Williams long range order parameter is defined as $S = r - w$.

For the cube corner site

$$w = .187$$

$$r = 1 - w = .813$$

..... a

For the face center site

$$w = \frac{.186}{3} = .062$$

$$r = 1 - w = .938$$

..... b

$$s = r - w = \frac{1}{4} (r - w)_a + \frac{3}{4} (r - w)_b$$

$$s = .81$$

This can be checked by finding the short range order parameter.

from Appendix 3:

$$Q_{BB} = \frac{N}{8} \left[12 - 6R + R^2 - (a^2 + b^2 + c^2 + d^2) \right] \quad \dots 9$$

$$Q_{AB} = \frac{N}{8} \left[24 - 2R^2 + 2(a^2 + b^2 + c^2 + d^2) \right] \quad \dots 10$$

$$F_A = \frac{1}{2} + \frac{1}{8} [a + b + c + d] \quad \dots 3$$

$$R = 8F_A - 4$$

Putting $a = b = c = d \neq a$ and equation for R into 9 and 10

$$Q_{AB} = \frac{N}{8} \left[24 - 2R^2 + 2(a^2 + 3b^2) \right]$$

$$Q_{BB} = \frac{N}{8} \left[12 - 6(8F_A - 4) + R^2 - (a^2 + 3b^2) \right]$$

Substituting $a^2 + 3b^2$ from Q_{BB} into Q_{AB} we get

$$\frac{Q_{AB}}{N} = 2 \left[6 - 6F_A - \frac{Q_{BB}}{N} \right] \quad \dots 16$$

But the number of manganese atoms in face center sites is $(.186)\frac{N}{4}$

and each of these has three manganese atoms as nearest neighbours.

$$\text{Therefore, } Q_{BB} = \frac{3(.186)N}{4} = 0.14 N$$

Substituting this into equation 16 and putting $F_A = \frac{3}{4}$

$$Q_{AB} = 2.72 N$$

$$\text{but } = \frac{q_{\text{max}} - q_{\text{rand}}}{q_{\text{max}} - q_{\text{rand}}}$$

$$\text{at } F_A = \frac{3}{4} \quad q_{\text{max}} = \frac{(Q_{AB})_{\text{ord}}}{6N}$$

$$q_{\text{rand}} = \frac{(Q_{AB})_{\text{dis}}}{6N}$$

Therefore, putting in the values of q_{max} and q_{rand} found from equation 13 and 15 of Appendix 3, we get

$$\sigma = 0.66 \quad \text{and } S = \sqrt{\sigma} = .79$$

This checks with the value of $s = .81$ found from the theory of Bragg and Williams.

When these calculations were repeated for heat treatment C,

the results were:

$s = 0.88$ from Bragg and Williams

$\sigma = 0.774$ and $s = 0.88$ from the short range order.

2. The calculation of the order parameter of Ni_3Mn from x-ray diffraction line intensities.

In this calculation the order domain size is assumed to be very large. For smaller domain sizes, this calculation would not be valid.

The intensity of an x-ray diffraction line is given by the equation:²³

$$I = \text{const.} \cdot p \cdot L \cdot e^{-2M} A(\theta) F^2 \quad \dots \dots \dots 17$$

where I = integrated intensity

F = structure amplitude factor

p = multiplicity factor

L = Lorenz and polarisation factor

e^{-2M} = Debye-Waller temperature factor

$A(\theta)$ = absorption factor

The individual factors will be calculated separately.

1. Multiplicity factor.

This factor is equal to the number of equivalent sets of planes with the same Miller indices.

$p = 12$ for the 110 plane

$p = 8$ for the 111 plane.

2. Absorption factor.

Taylor²³ gives the following formula for the angle between the incoming x-rays and the compact powder surface equal to φ :

$$A(\phi) = \text{const.} \frac{\sin(2\theta - \phi)}{\sin(2\theta - \phi) + \sin \phi}$$

In the Philips spectrometer $\phi = \theta$, therefore the absorption factor is independent of the Bragg angle θ .

3. Lorentz and polarisation factor.

Taylor²³ gives this factor equal to

$$L = \frac{1 + \cos^2 2\theta}{\cos \sin^2 \theta} \quad \text{for a polychromatic beam.}$$

For the (111) planes $L = 6.925$

For the (110) planes $L = 11.086$

4. Temperature factor.

$$M = \frac{3h^2}{mK\Theta} \left[\frac{\phi(x)}{x} + \frac{1}{4} \right] \frac{\sin^2 \theta}{\lambda^2}$$

h = Planck's constant in erg.sec

m = mass of atom in grams

K = Boltzmann's constant in erg deg⁻¹

Θ = Debye characteristic temperature

$x = \frac{\Theta}{T}$ where T is the absolute temperature

λ = wavelength in cm.

$\phi(x)$ = Debye function

θ = Bragg angle.

From the consideration of the Debye temperature for nickel and manganese, atoms with similar atomic number, and the melting points of these elements, the Debye temperature of Ni₃Mn was taken to be 340°K. This gave a value for the Debye function²⁴ of $\phi(x) = 0.749$.

The value of e^{-2M} for (110) plane is 0.9650

The value of e^{-2M} for (111) plane is 0.9485

5. Structure amplitude factor.

a. For face centered cubic lattices in general:

$$F = \sum_n f_n \cos 2\pi (hx_n + ky_n + lz_n)$$

where x, y, z are the co-ordinates of the atoms in the cell, hkl are the Miller indices for the plane under consideration, and f_n is the scattering factor of the atom at $x_n y_n z_n$.

For the 110 and 111 planes we get:

$$F_{110} = (f_1 - f_2)$$

$$F_{111} = (f_1 + 3f_2)$$

where f_1 is the mean atomic scattering factor for the cube corner sites, and f_2 is the mean atomic scattering factor for the face center sites.

The corrections for the atomic scattering factors of nickel and manganese for dispersion due to the k electrons were taken from James.²⁵

b. Effect of ordering on the structure factor.

The mean atomic scattering factor for any of the sublattices can be obtained from the order parameter and the values of the scattering factors corrected for dispersion due to k electrons.

Let the fraction of manganese atoms in face centered sites be P .

$$\left. \begin{array}{l} \text{At cube corner sites } w = P \\ r = 1 - P \end{array} \right\} \begin{array}{l} \dots \dots \dots a \\ \dots \dots \dots b \end{array}$$

$$\left. \begin{array}{l} \text{At face center sites } w = \frac{P}{3} \\ r = 1 - \frac{P}{3} \end{array} \right\}$$

$$S = \frac{1}{4} (r - w)_a + \frac{3}{4} (r - w)_b = 1 - P$$

From the values of r and w in terms of P , the values of f_1 and f_2 are:

$$f_1 = \left[(1 - P) f_{Mn} + P f_{Ni} \right]$$

$$f_2 = \left[\left(1 - \frac{P}{3}\right) f_{Ni} + \frac{P}{3} f_{Mn} \right]$$

Therefore

$$F_{111} = f_1 + 3 f_2 = f_{Mn} + 3 f_{Ni}$$

$$F_{110} = f_1 - f_2 = (f_{Mn} - f_{Ni}) \left(1 - \frac{4P}{3}\right)$$

6. Values for $\frac{I_{110}}{I_{111}}$

From the preceding values for the various factors in equation 17, we can find the ratio of $\frac{I_{110}}{I_{111}}$ in terms of P.

$$\frac{I_{110}}{I_{111}} = \left[1 - \frac{4P}{3}\right]^2 [.01230] \quad \dots \dots \dots 18$$

Taking the experimental value of I as the average number of counts when scanning across the line once, minus the average background, the following values are obtained for I_{110} and I_{111} from the measurements listed in the 'results'.

$$\begin{aligned} I_{110} &= \frac{\text{total no. counts} - \text{background}}{\text{no. oscillations}} \\ &= \left(\frac{74314 - 72670}{K \ 60} \right) (1.21) \end{aligned}$$

where K = angular velocity of scanning = $2^\circ (2\theta)$ per minute

1.21 = angle (2θ) per oscillation

60 = time of scanning in minutes.

In a similar manner I_{111} is found and

$$\frac{I_{110}}{I_{111}} = .0075 \pm .0016$$

This is equated to the theoretical value in equation 18 to find P and hence S. The value of S obtained is $S = 0.84 \pm 0.07$ where the probable error was calculated from the uncertainty in the results of the experimental intensity. It was assumed that all constants used were accurate.

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