Exchange-anisotropy field in disordered nickel-manganese alloys[a)]

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Magnetization data for disordered and weakly ordered Ni-Mn alloys from 22.1 to 32.1 at.% Mn have been obtained upon warming from 4.2 to 300 K, for measuring fields up to 100 kOe, after first cooling from 300 to 4.2 K in zero field or in 100 kOe. The measurements show that there is a minimum measuring field for which the data for zero-field cooling match the data for field cooling. This field, for the disordered alloy, increases from 10 kOe at 22.1 at.% Mn to 90 kOe at 32.1 at.% Mn. Partial atomic ordering reduces this coupling field. The coupling field is smaller than expected from previous studies. The data are qualitatively explained by a recently proposed local-environment model which considers explicitly the nearest-neighbor environment of Mn atoms in the alloy.

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I. INTRODUCTION

It has been almost 20 years since shifted hysteresis loops characteristic of exchange anisotropy were first observed in disordered Ni_3Mn alloys after cooling to a low temperature in an external field.[1] Several aspects of these early results, however, were not entirely explained by the simple exchange-anisotropy concept of distinct strongly coupled ferromagnetic and antiferromagnetic regions. First, hysteresis loops at 4 K after field cooling and zero-field cooling did not converge at moderate (10 kOe) fields as was expected.[1] Furthermore, pulsed fields of 140 kOe did not alter the exchange-anisotropy character.[2]

The present study of the magnetization of disordered Ni-Mn alloys was carried out over a wide range of field and temperature. Magnetization data after field cooling, in fields up to 100 kOe or in zero field, to 4 K were obtained for measuring fields up to 100 kOe in the temperature range 4 – 300 K. The data show that large measuring fields are as effective as field cooling in eliminating the characteristic drop in magnetization below 50 K. The minimum measuring field H_a ranges from 10 kOe for alloys with 22.1 at.% Mn to 90 kOe for 32.1 at.% Mn alloys. Weak partial ordering causes H_a to decrease.

These results show that the effective coupling field is smaller than previously believed. In addition, the data support a local-environment model which was recently proposed to explain the magnetic properties of disordered Ni-Mn alloys near the Ni_3Mn composition.[3,4]

II. EXPERIMENT

Ni-Mn alloy samples with compositions of 22.1, 24.6, 26.2, 29.0, and 32.1 at.% Mn were used in this study. The alloy samples were cast into ingots in an argon atmosphere after rf induction melting. The ingots were homogenized by cold working and quenching from 1000 °C several times. Spherical samples for measurement, 2.5 – 3.0 mm in diameter, were fabricated by a modified two-pipe lapidary method. Compositions were determined by atomic-absorption methods on pieces in close proximity to the region in the ingot from which the spherical samples were cut. The samples were atomically disordered by vacuum sealing them in thin-walled quartz tubes (3-mm inside diameter and 0.5-mm wall thickness), holding them at 1000 °C for 3 h and quenching in ice water. Thermocouple measurements indicated that the time spent in the ordering temperature range from 600 to 350 °C, during the quenching process, was about 3 sec. Neutron diffraction did not detect the presence of appreciable atomic order for rod samples quenched in this manner.[5]

Magnetization data were obtained with a vibrating sample magnetometer and a high-field solenoid capable of fields up to 100 kOe. In the magnetometer, the sample was oscillated at about 5 Hz with an amplitude of

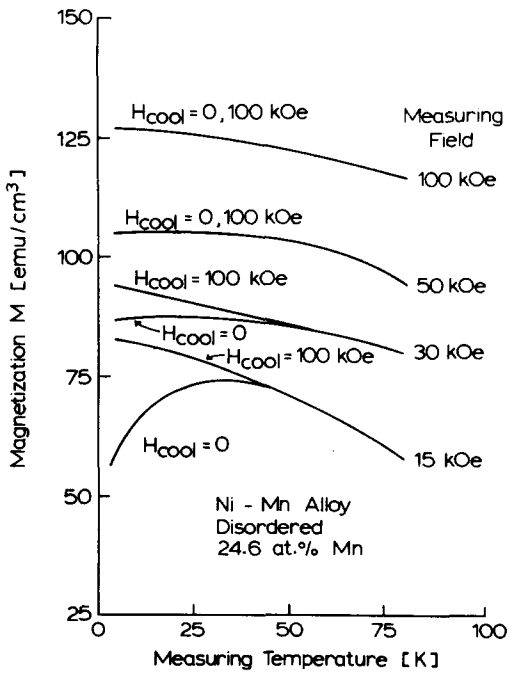

FIG. 1. Magnetization M versus temperature for a disordered 24.6 at.% Mn alloy upon warming from 4.2 K after initiallly cooling from room temperature to 4.2 K in 100 kOe (H_{cool} = 100 kOe) or in zero field (H_{cool} = 0), as indicated. Data were obtained for measuring fields of 15, 30, 50, and 100 kOe.

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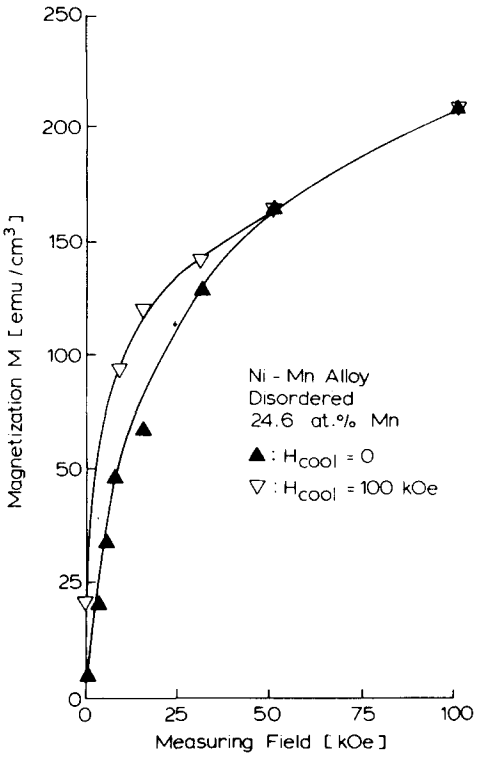

FIG. 2. Magnetization M versus measuring field for the 24.6 at.% Mn disordered alloy at 4.2 K after cooling from room temperature to 4.2 K in zero field (solid symbols) or in 100 kOe (open symbols).

about 3 mm by a mechanical-drive system powered by a synchronous motor. The sample motion was parallel to the applied field. The sample was centered between two pickup coils coaxial with the field. The ac signal from the coils was proportional to the magnetic moment of the sample. The system was calibrated by measuring the saturation moment of an iron sample with dimensions similar to the Ni-Mn samples. The sample and coils were placed in a variable-temperature Dewar and

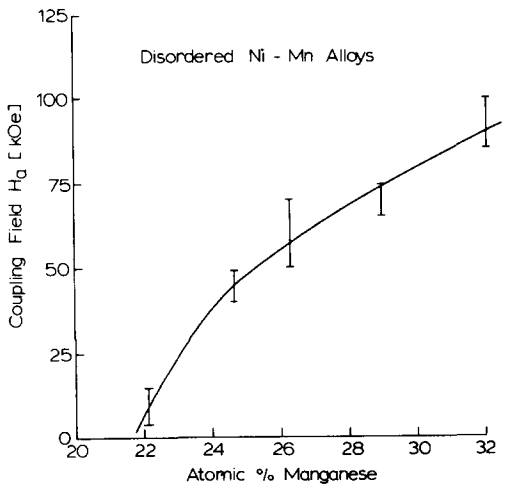

FIG. 3. Coupling field H_a, defined as the measuring field for which magnetization data at 4.2 K after zero-field cooling match the magnetization for field cooling. Cooling is from 300 to 4.2 K in a 100-kOe applied field. The field H_a is shown as a function of Mn content x in the alloy according to $Ni_{1-x}Mn_x$. Since only discrete cooling fields were used in this study, the range of possible H_a are indicated by vertical bars.

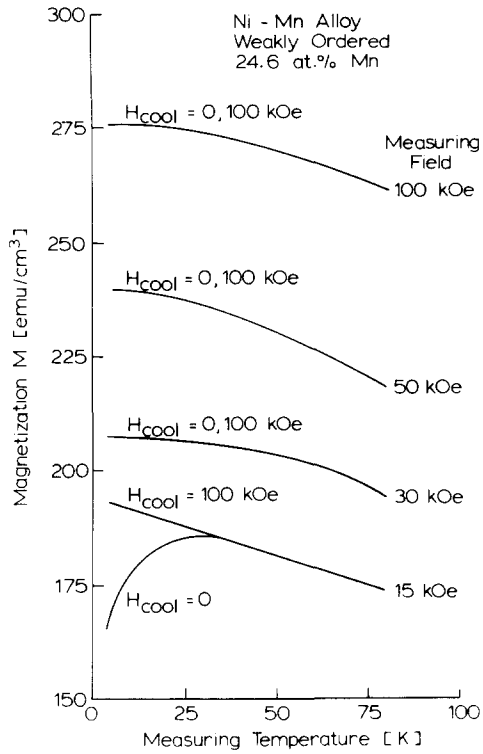

FIG. 4. Magnetization versus temperature for a weakly ordered 24.6 at.% Mn alloy upon warming from 4.2 K after initially cooling from room temperature to 4.2 K in 100 kOe ($H_{cool} = 100$ kOe) or in zero field ($H_{cool} = 0$), as indicated. Data were obtained for measuring fields of 15, 30, 50, and 100 kOe.

the temperature measured with a Au (Fe)-vs-Chromel thermocouple. Fields up to 100 kOe were supplied by a Bitter-type solenoid.[6]

III. RESULTS

Figure 1 shows curves of the magnetization M versus temperature T at measuring fields of 15, 30, 50, and 100 kOe after field cooling in 100 kOe ($H_{cool} = 100$ kOe or zero field ($H_{cool} = 0$) for the 24.6 at.% Mn alloy. Measurements were made as the temperature was increased above 4.2 K. Figure 1 illustrates the basic discovery that sufficiently high measuring fields, 50 kOe in this example, will produce identical M-vs-T curves, regardless of the field-cooling history. The qualitative explanation for the drop in M at low temperatures after zero-field cooling, as in the lowest curve in Fig. 1, has been in terms of a freezing-in of random magnetic order.[7] The present data show that whatever the microscopic details of that freezing process, applied fields on the order of 50 kOe are sufficient to pull those "frozen-in" regions into the field direction.

Figure 2 presents data for the 24.6 at.% Mn composition at 4 K. Values of the magnetization M versus measuring field are given after field cooling in 100 kOe and after zero-field cooling. The curves for field cooling in 100 kOe and zero-field cooling converge for measuring fields in excess of 50 kOe. The area between the two curves corresponds to a field-cooling anisotropy energy of about 6.6×10^5 erg/cm^3. Thus, an energy on

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the order of 10^5–10^6 erg/cm^3 and a field on the order of 50 kOe may be taken as measures of the strength of the coupling for spin freezing in disordered Ni_3Mn. Both curves in Fig. 2 are reversible.

Data were also obtained for other compositions. It was found that the minimum measuring field required to overcome the random spin freezing for zero-field cooling increases with Mn content. Figure 3 presents, in summary form, the results of these measurements on all compositions. The measuring field at which the zero-field-cooling curves converge with those for field cooling, denoted by H_a, is plotted as a function of Mn content for the disordered alloys. This field H_a is taken as the coupling field for the spin freezing. It is a strong function of composition. A 10% increase in Mn content results in an 80-kOe increase in H_a.

The data in Fig. 3 show that the coupling field increases with Mn content rather drastically. This suggests that Mn atoms in close proximity to each other may play a special role in the spin-freezing process. In order to test this hypothesis, a disordered 24.6 at.% Mn sample was annealed for 3 min at 500 °C to produce a small amount of short-range order and then measured. This would reduce the number of Mn pairs and, hence, might be expected to cause a decrease in H_a. Figure 4 shows the results. The coupling field, which was about 50 kOe for the disordered alloy, is reduced to less than 30 kOe by the brief anneal. This effect is related to the decrease in the number of Mn atoms in close proximity which results from the development of atomic order. The decrease in the coupling field for spin freezing with an increase in ordering is consistent with the effects of ordering in reducing the field-induced unidirectional anisotropy at low temperatures.[8] Note also that the increase in ordering increases M. This is also due to the decrease in the concentration of antiferromagnetically coupled Mn pairs with the development of atomic ordering.

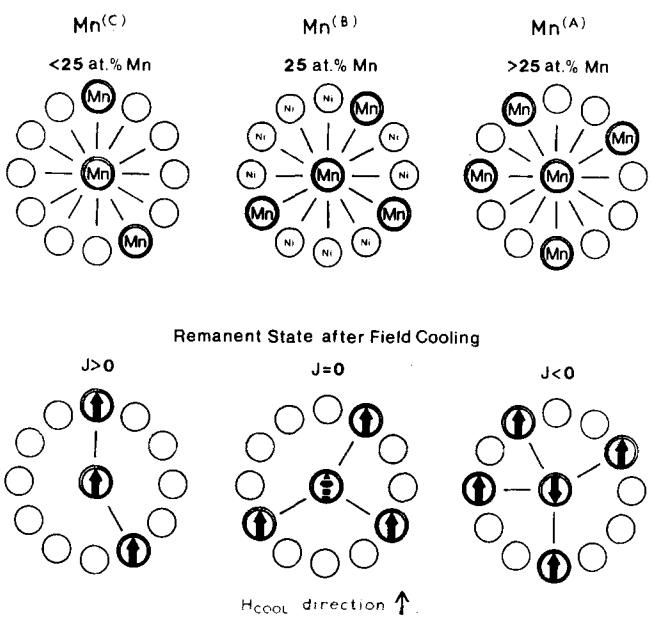

FIG. 5. Schematic illustration of the three types of Mn core atoms, as classified by their nearest-neighbor environments. The upper diagrams indicate the atomic environment. The lower diagrams indicate the spin order proposed after field cooling.

IV. DISCUSSION

The present results on the effects of cooling-field history and measuring field on the temperature dependence of the magnetization are noteworthy in that they demonstrate (1) a coupling field H_a for spin freezing which is much weaker than expected on the basis of the accepted model[9,10], (2) a strong composition dependence for H_a in the disordered alloys near the Ni_3Mn composition, and (3) a sensitive dependence of H_a on the degree of atomic order.

A local environment model (LEM) was recently proposed to explain the low-field (0–8) kOe magnetization in disordered alloys[3] and a new remanence reversal effect in weakly ordered alloys.[4] This LEM also appears to qualitatively explain the present experimental results. In the LEM, Mn atoms are classified according to their nearest-neighbor environment (NNE). Three different types, $Mn^{(A)}$, $Mn^{(B)}$, and $Mn^{(C)}$, are illustrated in Fig. 5. One type, $Mn^{(A)}$, has a Mn-rich NNE and is coupled antiferromagnetically to its Mn nearest neighbors. These $Mn^{(A)}$ aggregates have a relatively high Néel temperature. The second type, $Mn^{(B)}$, has a NNE corresponding to a local composition of 25 at.% Mn. The $Mn^{(B)}$ is exposed to a relatively weak molecular field. For this reason, the core Mn atom is shown with a tentative moment direction. The third type, $Mn^{(C)}$, has a Mn-deficient NNE and is ferromagnetically coupled to its Mn and Ni nearest neighbors. The separation into three categories is rather arbitrary and is done primarily to illustrate the basic mechanisms. The Mn atoms have, of course, a statistical distribution of nearest-neighbor environments. For purposes of discussion, it is assumed that each Mn atom in the NNE is of the $Mn^{(B)}$ variety for Mn contents in the 25 at.% range considered here.

$Mn^{(A)}$ atoms are those Mn atoms which have four or more nearest-neighbor Mn atoms in their nearest-neighbor environment (NNE). Figure 5 shows a core $Mn^{(A)}$ atom with four such neighbors; the remaining atoms in the NNE are nickel atoms. It is assumed that when the Mn NNE contains four or more Mn atoms as for $Mn^{(A)}$, the NNE magnetic moments are (1) coupled parallel within themselves and (2) coupled antiparallel to the core $Mn^{(A)}$ atom. This assumption is plausible since (1) the Mn atoms in NNE are mostly $Mn^{(B)}$ and (2) nearest-neighbor Mn atoms have an antiferromagnetic exchange interaction, and sufficient Mn atoms in the NNE should cause this tendency to dominate over the ferromagnetic Ni-Mn nearest-neighbor exchange. The presence of Mn spins coupled antiparallel to their environmental spins has been directly observed using NMR techniques by Kitaoka and Asayama.[11] Thus, the $Mn^{(A)}$ regions may be viewed as a ferromagnetic Mn-rich NNE shell which is coupled antiferromagnetically to the $Mn^{(A)}$ core atom.

The situation becomes more complex when the number of Mn atoms becomes large. If Mn atoms in the NNE of the core $Mn^{(A)}$ atom are also in each other's NNE, the

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NNE of the core is not likely to be simply ferromagnetic. A quantitative LEM calculation should take this into consideration since the Mn content is not dilute in these samples. In the present qualitative discussion of exchange anisotropy, this complication is ignored.

The interactions within $Mn^{(A)}$ regions can be used to qualitatively explain the magnetization data of Sec III, including the differences between the magnetization-vs-temperature curves for field cooling and zero-field cooling and the composition and order dependencies of the coupling field H_a. An atomic site in the fcc lattice which contains a manganese atom with n nearest-neighbor manganese atoms will occur with a probability

$$P_{Mn}(n) = x[12!/n!(12-n)!](1-p)^n p^{12-n}. \quad (1)$$

In Eq. (1), p is the probability that a given core Mn nearest-neighbor atom will be a Ni atom, and x is the fraction of Mn atoms per formula unit, $Ni_{1-x}Mn_x$.

The probability p is related to a short-range-order parameter σ,

$$\sigma = (p - p_{disord})/(p_{ord} - P_{disord}). \quad (2)$$

The subscripts disord and ord refer to the probability that a given manganese nearest neighbor is nickel for disordered and perfectly ordered alloys, respectively. These probabilities are given by

$$p_{ord} = 1, \quad x \leq 0.25 \quad (3a)$$

$$p_{ord} = 1.25 - x, \quad x \geq 0.25 \quad (3b)$$

$$p_{disord} = (1 - x). \quad (4)$$

From relations (1)—(4), the existence probability of a Mn atom with different NNE can be calculated as a function of composition x and short-range-order parameter σ. The probability that any atomic site on the fcc lattice is a $Mn^{(A)}$ site is given by

$$P_{Mn^{(A)}}(x, \sigma) = \sum_{n=4}^{12} P_{Mn(n)}(x, \sigma), \quad (5)$$

the existence probability for a Mn atom with four or more nearest-neighbor Mn atoms. For stoichiometric-disordered Ni_3Mn with $\sigma = 0$, one obtains $P_{Mn(A)}(0.25, 0) = 0.087$. Note that each $Mn^{(A)}$ core atom holds a significant number of nearest-neighbor Mn atoms (4 – 12) in parallel orientations (Fig. 5). It is reasonable that the $Mn^{(A)}$ regions can possess sufficient net moment to account for the different magnetizations upon field cooling and zero-field cooling at low measuring fields.

The specific processes that occur during field cooling are proposed as follows:

(1) There exist $Mn^{(A)}$ regions in which the NNE is essentially ferromagnetic and is coupled antiferromagnetically to the core $Mn^{(A)}$ atom.

(2) In an applied field, these NNE moments will be aligned with that field.

(3) When, during field cooling, the temperature drops below the freezing temperature, the $Mn^{(A)}$ core moment freezes in antiparallel to the NNE moments.

(4) Below the freezing temperature, the NNE moments will tend to be parallel to the direction of the initial cooling field because of their antiferromagnetic coupling to the frozen-in $Mn^{(A)}$ core moment.

For zero-field cooling, one has essentially the same situation as for field cooling except that the $Mn^{(A)}$ units freeze in with random orientations relative to each other. One expects a distribution in freezing temperatures for the different NNE configurations associated with $Mn^{(A)}$ cores. Below the freezing temperature, the $Mn^{(A)}$ core moments remain locked in their orientations.

The model shows why the curves in Fig. 2 are reversible in character and why the coupling should decrease with an increase in ordering or a reduction in Mn content. Consider Fig. 5 once more under conditions of zero-field cooling. The $Mn^{(A)}$ regions freeze in randomly. Assume that the core $Mn^{(A)}$ atom remains frozen under the application of the measuring field, but that the ferromagnetic NNE with a relatively large net moment will be strongly influenced by the field. For some sufficiently high measuring field, the NNE moment will be rotated into the field direction against the influence of the exchange coupling to the $Mn^{(A)}$. If the field is reduced, the NNE will relax back to its antiparallel orientation. The result is a reversible effect, and there is a correlation between the field which overcomes the exchange coupling and the observed convergence field H_a. Finally, the entire process depends critically on the population of $Mn^{(A)}$ regions in the alloy. This population increases with Mn content and decreases with the development of order. The convergence field H_a exhibits both dependencies as well.

From Fig. 2, the energy of the antiparallel coupling is on the order of 5×10^5 erg/cm^3 for the 24.6 at.% Mn alloy. Previous data on the unidirectional anisotropy from low-field (12 kOe) torque measurements[8] indicate order-of-magnitude agreement. The results indicate, therefore, that the exchange anisotropy is a first-order effect of the $Mn^{(A)}$ regions in the local-environment model.

Several comparisons may be made between this mechanism and the classic exchange-anisotropy studies of ferromagnetic cobalt particles coated with antiferromagnetic cobalt oxide.[9] In that system, macroscopic regions interact magnetically through a surface boundary. In the present case, the entire region is microscopic, on the order of a few atomic spacings. It is also important to note the differences between the present LEM and the macroscopic exchange-anisotropy concept. In the $Mn^{(A)}$ regions, both components (the core $Mn^{(A)}$ atom and the NNE) have net moments. For proper temperature dependencies of the NNE and $Mn^{(A)}$ core magnetizations, one would expect to see a compensation point in the remanence. In fact, a closely related remanence-reversal effect was recently reported.[4]

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