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Nuclear-Magnetic-Resonance Studies of Mn^{55} in Ordered Ni_3Mn

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Nuclear-magnetic-resonance studies of Mn^{55} as well as bulk magnetization measurements have been carried out on Ni_3Mn samples having various degrees of order. The results are interpreted in terms of long-range-ordering theory and neighbor contributions to the hyperfine fields. A theoretical expression for the magnetization as a function of order is given, which is valid for values of the long-range-order parameter S in the range 0.6–1.0. An NMR line at −370 kG is identified with Mn^{55} in a well-ordered environment. Other lines are attributed to incompletely ordered sites. Consideration of the difference between the resonance of the well-ordered Mn and that of dilute Mn in Ni leads to values for next-nearest-neighbor as well as nearest-neighbor effects on the hyperfine field. The effect of temperature on the spectra is attributed, in part, to average exchange interactions being different for different environments.

I. INTRODUCTION

The order-disorder transformation which occurs in Ni-Mn alloys whose composition is approximately Ni_3Mn has been extensively studied for several decades.[1–6] The magnetic properties are of particular interest. In the disordered alloy, since the Mn-Mn exchange interactions are antiferromagnetic, the Mn atoms are roughly paired off and the magnetization of the alloy is quite small. As the alloy becomes ordered, Mn atoms tend to see only Ni nearest neighbors and the alloy becomes strongly ferromagnetic, with a resulting marked increase in the magnetization of the alloy.

Studies of the nuclear magnetic resonance (NMR) of Mn^{55} in disordered Ni-Mn alloys in the composition range 1–20% Mn have been reported previously.[7,8] In the present investigation, we have studied the Mn^{55} NMR in a sample with composition near Ni_3Mn subjected to different ordering treatments. The saturation magnetization in the same samples has also been studied in order to ascertain the degree of order.

In Sec. II, the experimental techniques and results are discussed; in Sec. III, the effects of ordering on the hyperfine fields at the Mn^{55} nuclei and on the magnetic properites are discussed.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

A. Sample Treatment

An approximately stoichiometric alloy of Ni_3Mn (actually 25.5 at.% Mn) was prepared by arc melting and water quenching, which initially resulted in a substantially disordered structure. The material was filed into particles less than 50 μ in diameter and mixed with Al_2O_3 powder to prevent sintering. The mixture was divided into three portions, each of which was subjected to vacuum annealing for different lengths of time. The first sample was brought to 430 °C in a few hours and annealed for one day. The annealing time for the second sample was five days. The third sample was treated according to the following prescription by Piercy and Morgan[2]: 16 h at 555 °C, 250 h at 490 °C, 260 h at 420 °C, and 250 h at 400 °C, for a total of 32 days. After annealing, the Al_2O_3 was removed magnetically.

B. NMR Equipment and Techniques

The zero-field NMR spectrum of the Mn^{55} nuclei was studied by the spin-echo technique, the intensity of the echo being recorded as a function of frequency. The equipment and technique were essentially the same as used in previous studies.[9,10]

Strictly speaking, one should divide the recorded integrated intensities by a factor ν^2, where ν is the frequency of the line, to account for the fact that the nuclear signal induced in the sample coil is proportional to the frequency, and to account for the increased nuclear polarization at higher frequencies. This correction was not applied, since it is not crucial for the identification of resonance peaks. The measurements at 4.2 °K were carried out with an exposed-tip helium Dewar.

C. NMR Results

The NMR results at 4.2 °K are presented in Fig. 1 for the untreated powder as well as for the annealed samples. In each case, the highest observed signal is assigned unit intensity. Figure 2 shows the corresponding results at 77 °K, except that the unannealed sample was too weak to be observed.

D. Measurements of Bulk Magnetism

The magnetization at room temperature was plotted as a function of magnetic field up to 15 kG, and the linear portion extrapolated to zero field. The results are given in Table I.

III. DISCUSSION

A. Dependence of Magnetic Properties on Ordering

Before discussing the hyperfine fields, we will consider the interpretation of the bulk magnetism with respect to atomic ordering, which has been treated by Marcinkowski and Poliak.[4] By hypothesizing reasonable values for the Mn-Ni and Ni-Ni nearest-neighbor exchange interactions, they conclude that a given Mn will become antiferromagnetically aligned with respect to its neighbors if the nearest-neighbor shell contains three or more ferromagnetically aligned Mn atoms. Therefore, in the fully disordered alloy, where most of the Mn atoms have three or more Mn nearest neighbors, the Mn atoms are nearly paired off and the resultant magnetization is small.

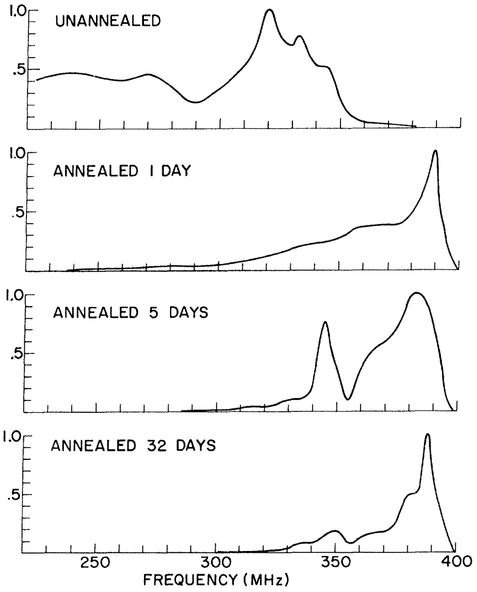

FIG. 1. Uncorrected Mn^{55} line shapes at 4.2 °K.

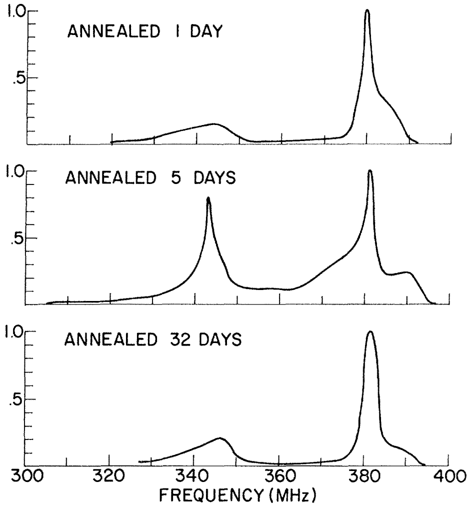

FIG. 2. Uncorrected Mn^{55} line shapes at 77 °K. The unannealed signal was to weak to observe.

In the completely ordered state, each Mn atom has all 12 nearest-neighbor sites occupied by Ni atoms, and the ferromagnetically aligned Mn atoms result in a large magnetization. For moderate departure from perfect order, we may assume that the number of antiferromagnetically aligned atoms can be approximately determined from the Bragg-Williams long-range parameter S. In particular, the great majority of Mn atoms on Mn sites will be ferromagnetically aligned, while the great majority of Mn atoms on Ni sites will be antiferromagnetic, since the latter site normally has four Mn nearest neighbors. In the notation of Cowley,[11] the fractions of Mn atoms on Mn sites and on Ni sites are r_β and $1 - r_\beta$, respectively, where $r_\beta = 4m_A m_B S + m_B$; m_A, the fraction of Ni

TABLE I. Measured magnetization per gram σ at room temperature (extrapolated to zero field) for samples subjected to the various annealing procedures described in text. Magnetization in terms of $4\pi I$ is also given along with the long-range-order parameter S deduced from magnetization values.

Total annealing time (days)	σ $\left(\frac{\text{G cm}^3}{\text{g}}\right)$	$4\pi I$ (Oe)	S
Unannealed	0.84	90	...
1	32.8	3500	0.64
5	48.5	5150	0.74
32	70.1	7460	0.88

atoms, is $\frac{3}{4}$; and m_B, the fraction of Mn atoms, is $\frac{1}{4}$. If $c_\uparrow$ and $c_\downarrow$ denote the fractions of ferromagnetically and antiferromagnetically aligned Mn, respectively, the net value $c_\uparrow - c_\downarrow$ is given by

$$c_\uparrow - c_\downarrow = r_\beta - (1 - r_\beta) = \tfrac{1}{2}(3S - 1). \tag{1}$$

If, as previously,[8] we assume that only Mn moments can be antiferromagnetically aligned, the average magnetic moment per atom in Ni_3Mn alloy can be written as

$$\overline{\mu} = 0.25\,\mu_{\mathrm{Mn}}\,(c_\uparrow - c_\downarrow) + 0.75\,\mu_{\mathrm{Ni}}\ . \tag{2}$$

Here μ_{Mn} and μ_{Ni}, the Mn and Ni magnetic moments, are assumed to have the fully ordered values[12] of 3.2 μ_B and 0.3 μ_B, respectively.

Combining Eqs. (1) and (2), we have

$$\overline{\mu} = 1.2S - 0.175, \tag{3}$$

which is plotted in Fig. 3 along with the experimental points of Doroschenko,[5] who performed magnetization measurements on nearly stoichiometric Ni_3Mn alloy. The agreement is satisfactory for high values of S, where the simple theory is expected to be adequate. Although the magnetic moments in Ni_3Mn have been measured only in the fully ordered case, apparently our use of these values as the order decreases does not seriously affect the analysis. The Mn moment is probably not a strong function of disorder.

On account of the relation between order and magnetization, we can estimate S for our samples from our magnetization measurements. The room-temperature extrapolated magnetization values are given in Table I. Using Doroschenko's results,[5] we plotted $4\pi I$ versus S, which turned out fairly linear over the range $S = 0.6-1.0$. From this, the values of S corresponding to the magnetization of our samples were derived and entered in Table I.

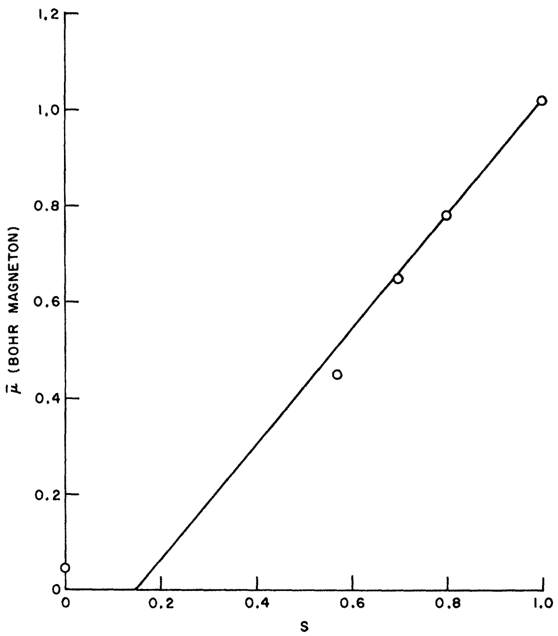

FIG. 3. Average magnetic moment per atom in Ni_3Mn as a function of long-range-order parameter S according to Eq. (3). The five experimental points are from Ref. 5.

B. Hyperfine Fields

As was done in the previous discussions[8] of Ni alloys, we have used a phenomenological approach and tried to fit the hyperfine fields to an expression of the form

$$H_A = a\mu_A + b\overline{\mu}\ . \tag{4}$$

Here the first term represents the contribution to the hyperfine field H at the nucleus of atom A from the magnetic moment μ_A of the parent atom, and $\overline{\mu}$ represents the average magnetic moment of the alloy, or in a more detailed treatment the average moment of neighboring atoms.

Previous studies of Ni alloys indicate that both a and b are negative and of comparable magnitude. In nickel-maganese alloys, a and b were shown to be about -100 and -50 kG/μ_B, respectively.[8] For dilute Mn in Ni, $\mu_{\mathrm{Mn}} = 3.0\ \mu_B$, while $\overline{\mu} = 0.6\ \mu_B$.[8] Equation (4) would then yield a value of -330 kG (corresponding to a Mn^{55} frequency of 347 MHz) in agreement with previous NMR studies of dilute Mn^{55} in Ni. Consider now the spectra of Fig. 1. For the unannealed alloy where $S \approx 0$, we expect the Mn atoms to be roughly paired off so that a given Mn atom will see Mn near neighbors which are predominantly antiferromagnetically aligned. This will cause $\overline{\mu}$ (assuming it to be related to the $\overline{\mu}$ of neighboring atoms) to be of opposite sign to μ_A with a resultant decrease in the absolute value of the hyperfine field relative to the value for Mn added dilutely to Ni. This is consistent with the observed spectra for the unannealed sample.

In ordered spectra at 4.2 °K there are prominent lines at 390 MHz and at 345–350 MHz. Both lines decrease in frequency as an external magnetic field is applied. Since the hyperfine field is negative, both resonances are due to a Mn atom whose spin is oriented along the magnetization direction. (Thus, a Mn in a Ni position, which would be oppositely aligned with respect to the three or four nearest-neighbor Mn atoms, could not be involved.) The fact that the 390-MHz line predominates in the best-ordered sample suggests that it is due to a Mn atom in a perfectly ordered environment, i.e., all 12 nearest neighbors being Ni and all six next nearest neighbors being Mn. This is also supported by the fact that this line decreases to 381 MHz at 77 °K and 370 MHz at room temperature, which makes the resonance frequency of the line nearly proportional to the saturation magnetization of the fully ordered alloy as measured by Marcinkowski and Brown.[3] This indicates that the line is due to Mn atoms in an ordered or nearly ordered configuration.

Since the 350-MHz line agrees closely with the frequency of dilute Mn in Ni, which has Ni next nearest as well as nearest neighbors, we will tentatively suppose that this resonance is due to regions in which short-range order obtains, but not long-range order. According to Marcinkowski and Brown,[3] annealing at temperatures below 425 °C causes transition from disorder to long-range order without the appearance of short-range-order regions. Perhaps our heat treatment was not well enough regulated to preclude the short-range-order phase.

If it is assumed that the influence of the neighbors on the hyperfine field can be accounted for by the first two neighbor shells, which have, respectively, 12 and 6 atoms, we can write

$$H_A = a\mu_A + 12b_1\mu_1 + 6b_2\mu_2 . \tag{5}$$

If the constants $a = -100\ \mathrm{kG}/\mu_B$, b_1, and b_2 are independent of order and concentration, b_1 and b_2 can be determined from the resonant field at -330 kG in the dilute-Mn-in-Ni sample and the well-ordered line at -370 kG. For the dilute line, $\mu_A = 3.0\ \mu_B$, $\mu_1 = \mu_2 = \mu_{\mathrm{Ni}} = 0.6\ \mu_B$; and for the well-ordered line, $\mu_A = 3.2\ \mu_B$, $\mu_1 = \mu_{\mathrm{Ni}} = 0.3\ \mu_B$, and $\mu_2 = \mu_{\mathrm{Mn}} = 3.2\ \mu_B$. The resulting equations

$$-330 = -300 + 7.2b_1 + 3.6b_2 ,$$

$$-370 = -320 + 3.6b_1 + 19.2b_2$$

can be solved to obtain $b_1 = -3.2$ and $b_2 = -2.0\ \mathrm{kG}/\mu_B$. If these values of b_1 and b_2 were reliable, one should be able to account for the satellite line at 360 MHz, which appears in dilute Mn in Ni. Since this is expected to be due to a single nearest-neighbor position being occupied by a Mn instead of Ni, the increase of frequency would be $(3.0-0.6)\times 3.2 = 7.7$ kG, or 8.1 MHz, rather than the observed 13 MHz. This inadequacy is, however, not surprising since, in addition to the theoretical simplifications, the values of the Mn moments as a function of order have considerable errors.

The weaker resonances in the 4.2 °K spectra lying between the 350-MHz and 390-MHz lines must be due to Mn atoms whose environments are not well ordered. For example, consider a Mn atom trading places with a nearest-neighbor Ni in an otherwise well-ordered region, thus leaving only three Mn atoms in the four normal Mn nearest-neighbor sites surrounding the misplaced Mn atom. Since the latter atom will be aligned opposite to $\overline{\mu}$, each of the three Mn atoms surrounding it will have one nearest-neighbor magnetic moment of $-3.2\ \mu_B$ rather than $0.3\ \mu_B$, thus lowering the resonant frequency with respect to the well-ordered line. Note, however, that at 77 °K this resonance disappears. This can be understood by referring to Table II, which shows the estimated average exchange integral $\overline{J}$ associated with a central Mn atom surrounded by various numbers of Ni and Mn atoms according to Marcinkowski and Poliak.[4] If we associate the Curie temperature of the fully ordered alloy (i.e., 728 °K) with the zero-Mn-neighbor cluster which has $\overline{J} = 1.00 J_{\mathrm{NiMn}}$, then we may estimate the effective Curie or Nẽel points for the other neighbor configurations by taking them proportional to $|\overline{J}|$, and these are also listed in Table II. Since the misplaced Mn atom has three Mn neighbors, it has $(T_c)_{\mathrm{eff}} = 58$ °K, and at 77 °K it no longer remains aligned with respect to $\overline{\mu}$, and no longer depresses the hyperfine field. Thus, at 77 °K this lower resonance would disappear, just as indicated by the observed spectrum at this temperature.

Previously, investigations have been made of the effect of order in $\mathrm{MnNi_3}$ upon the hyperfine field by the method of nuclear specific heats.[13,14] The results of Ref. 13 lead to values of the average hyperfine field as high as 490 kG for their best-ordered sample. This is in disagreement with our results, since no resonance was observed in this region. Our data, however, are reasonably consistent with the much lower hyperfine fields reported in Ref. 14. The value for their best-annealed sample (900 h) was 335 kG, while from our Fig. 1 we estimate an average value of 355 kG, if the v^2 correction is applied. For the unannealed sample, they give 259 kG, which appears comparable to the corresponding spectrum in our Fig. 1, although the exact low-frequency cutoff of our spectrum was not measured. Thus, our results tend to confirm those of Ref. 14, and it appears that the excessively high values of Ref. 13 are due to their method of fitting the heat-capacity-versus-temperature curves.

IV. CONCLUSIONS

NMR measurements of $\mathrm{Mn^{55}}$ display hyperfine fields in $\mathrm{Ni_3Mn}$ corresponding to various near-neighbor configurations depending on the degree of order. These measurements, done at both 4.2 and 77 °K, give a more detailed picture of the ordering process, whereas previous nuclear-specific-heat

TABLE II. Average exchange integral $\overline{J}$ and effective Curie temperature $(T_c)_{\mathrm{eff}}$ associated with a central Mn atom surrounded by various number of Mn and Ni nearest neighbors.

Number of Mn neighbors	$\overline{J}$ (J_{NiMn})	$(T_c)_{\mathrm{eff}}$ (°K)
0	1.00	728
1	0.63	460
2	0.28	204
3	−0.08	58
4	−0.45	328

measurements have yielded conflicting, and at best, average values for the hyperfine field.

The results of this investigation together with previous results on dilute Mn in Ni are combined to separate the nearest- and next-nearest-neighbor contributions to the hyperfine field. The values obtained are -3.2 kG/μ_B for a nearest neighbor and -2.0 kG/μ_B for the next nearest neighbor. However, those values should be viewed with considerable caution, on account of uncertainties inherent in their derivation.

Computation of ferromagnetically and antiferromagnetically aligned Mn atoms from the long-range-order parameter S is shown to predict the bulk magnetization satisfactorily in the range $S = 0.6 - 1.0$.

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Nuclear Magnetic Resonance of ^{15}N in the Paramagnetic State of Enriched Uranium Mononitride ($U\,^{15}N$)†

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Nuclear-magnetic-resonance (NMR) measurements were made on ^{15}N in the paramagnetic state of enriched $U^{15}N$. The Knight shift K and the linewidth in $U^{15}N$ were measured under similar conditions as in previous NMR measurements on $U^{14}N$, except that in $U^{15}N$ the observed dispersion lines were distorted and broadened experimentally. Although the K values in $U^{15}N$ are slightly lower than those in $U^{14}N$, their dependence on the molar susceptibility χ_M, $K = K_0 + \alpha\chi_M$, is nearly the same, with a slope $\alpha(U^{15}N) = 3.8 \pm 0.4$ mole/emu instead of $\alpha(U^{14}N) = 4.20 \pm 0.25$ mole/emu, and with similar K_0 values. The different χ_M data in the literature and their effect on K_0 and K are attributed to variations in stoichiometry and substitutional impurities among the samples.

I. INTRODUCTION

In a previous paper,[1] continuous-wave (cw) nuclear-magnetic-resonance (NMR) measurements on ^{14}N in the paramagnetic state of uranium mononitride (UN) were reported and discussed in terms of the magnetic and electronic properties of UN. The Knight shift K and linewidth ΔH were related to the available data of the molar susceptibility χ_M, obtained by Trzebiatowski *et al.*[2] and by Albutt *et al.*[3] The two sets of data were in fair agreement with each other, and approximately represented by a Curie-Weiss behavior.

The Knight shift of ^{14}N in UN in the temperature range of 77 – 300 °K was found to be linear in χ_M,

$$^{14}K = -(31.5 \pm 3.5) \times 10^{-4} + (4.20 \pm 0.25)\chi_M, \qquad (1)$$

when the available χ_M data from Refs. 2 and 3 were used. Equation (1) has the general form of K versus χ_M in the paramagnetic state,