Similarly low values of $\delta$ and large values of $f$ are obtainable from the data on trivalent iron in oxygen-deficient perovskites, $BaFeO_{3-x}$ and $SrFeO_{3-x}$.[23]

## ACKNOWLEDGMENTS

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[23] From the spectra of Refs. 7–9, it must be inferred that there are quadrupole-split lines for the trivalent Fe ions. This is necessary so as to obtain a proper isomer shift and also to account for the proximity of oxygen-deficient sites. From the relative areas of the absorption dips for the unsplit $Fe^{4+}$ line and the split $Fe^{3+}$ lines, it becomes evident that the recoilless fraction from the vacancy-associated $Fe^{3+}$ ions is larger than expected from its chemical proportion.

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# Nuclear-Resonance Spin-Echo Study of $^{61}$Ni Hyperfine Fields in Ferromagnetic Ni-Al, Ni-V, and Ni-Cr Systems

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The nuclear-magnetic-resonance line shapes of $^{61}$Ni have been studied in ferromagnetic Ni-rich Ni-Al, Ni-V, and Ni-Cr powders by plotting the spin-echo amplitude as a function of frequency across the inhomogeneously broadened resonance lines. The measurements were made at 4.2°K in alloys containing concentrations of up to 12.3 at.% Al, 5.5% V, and 5.3% Cr. In all three systems, the average hyperfine fields decreased approximately linearly with increasing solute concentration. A general discussion of the relationship between the average hyperfine field and the atomic moments is presented. The major contribution to the hyperfine field is believed due to the moment on the parent atom, with a smaller contribution from moments on neighboring atoms via conduction-electron polarization. The detailed structure of the resonance spectra is analyzed. It is found that the magnetic disturbances are spatially more widespread in the Ni-Al and,Ni-V systems than in the Ni-Cr system. The Ni-Cr system in turn has a more delocalized behavior than the Ni-Co system previously studied. The results in the Ni-V and Ni-Cr systems are consistent with results obtained by Collins and Low using neutron scattering techniques.

## I. INTRODUCTION

THE magnetic properties of the 3*d*-transition metals and alloys have been subjects of interest for many years. Many experimental techniques have been employed in studying the magnetic properties of these materials. Saturation magnetization measurements have been used in order to better characterize the electronic structure of these materials. In recent years neutron-scattering, Mössbauer-effect and nuclear-magnetic-resonance techniques have been used extensively in studying the microscopic magnetic properties of the transition-metal alloys.

Saturation-magnetization measurements only provide information about the average magnetic moments of the alloys. The average-magnetic-moment measurements are summarized by the well-known Slater-Pauling curve. Neutron-scattering techniques have been used to determine the magnetic moment distributions about the solute atom in several binary ferromagnetic systems. In some systems it has also been possible to estimate the magnetic moments on the host atoms which are near neighbors to a solute atom, using these techniques. Nuclear-magnetic-resonance techniques and the Mössbauer effect have also been successfully used to measure the nuclear-magnetic-hyperfine fields in many binary systems. A detailed study of the hyperfine fields in these alloys gives information about both the 3*d* atomic moments and the conduction-electron polarization. Thus, the information derived from these different experimental techniques taken together provide a more complete picture of the magnetic properties of these materials.

In a previous paper,[1] the authors have reported the results of a nuclear-resonance spin-echo study of the hyperfine fields at both the Ni and Co sites in Ni-rich Ni-Co alloys, a system which falls on the right branch of the Slater-Pauling curve. In this paper we present results of a similar study of the Ni hyperfine fields in Ni-rich Ni-V, Ni-Cr and Ni-Al alloys. These systems deviate from the right branch of the Slater-Pauling curve. The Ni-Al system has been studied for concentrations containing up to 12.3% Al (all percentages are atomic), the Ni-V system for concentrations up to 5.5%

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[1] R. L. Streever and G. A. Uriano, Phys. Rev. **139**, A135 (1965).

V and the Ni-Cr system for concentrations up to 5.3% Cr. We have determined the distribution in hyperfine fields in these alloys by measuring the amplitude of the spin-echo signal as a function of frequency across the inhomogeneously broadened resonance line.

In Sec. II the experimental methods are discussed, and in Sec. III the results are presented and discussed. An attempt is made to correlate the nuclear-resonance results obtained in this study with those obtained from the previous Ni-Co study and with saturation-magnetization measurements in Ni-Al,[2,3] Ni-V[2,3] and Ni-Cr.[2–4] A correlation with neutron-scattering results[5,6] is also made for the Ni-Cr and Ni-V systems.

## II. EXPERIMENTAL

### A. Samples

The samples used in the work were prepared by induction heating the appropriate amounts of the constituent elements. The following samples were used in the study: Ni-Al in concentrations of 1.9, 5.2, 8.1, and 12.3%; Ni-V in concentrations of 1.3, 1.9, 3.2, and 5.5%; and Ni-Cr in concentrations of 0.4, 2.5, 3.3, and 5.3%. These concentrations were confirmed by chemical analysis. The 1.9- and 5.2% Al, 1.3 and 1.9% V and 0.4- and 2.5% Cr alloys were sprayed into fine particles 10 $\mu$ or less in diameter. The higher concentration alloys were cast into ingots and then filed into fine particles 50 $\mu$ or less in diameter. None of these samples were annealed because, as discussed in the previous paper,[1] the resonance line shapes seem to be independent of annealing. Also, the strong signal believed due to "electronic" losses in the sample was suppressed by using the unannealed samples.

### B. Equipment and Measurement Techniques

The nuclear resonances were studied using the free-precession method, where the amplitude of the spin-echo signal has been plotted as a function of frequency across the inhomogeneously broadened line. The spin-echo spectrometer used in these measurements as well as the basic measurement techniques has been described in detail previously. However, in these measurements pulses were used to calibrate the sensitivity of the equipment. The pulses were obtained by pulse modulating the VHF standard signal generator which was inductively coupled to the pickup coil of the pulsed oscillator. Proper matching insured that a calibrated voltage independent of frequency was induced in the pickup coil. At each frequency, the calibrated pulse was made equal to the amplitude of the echo signal, both being observed on an oscilloscope. The calibrated pulse voltage was taken to be the amplitude of the nuclear signal.

Several corrections must be made to the experimental line shapes in order to determine the true line shape. The amplitude of the spin-echo signal (emf) induced in the pickup coil in a free precession experiment is proportional to the time derivative of the macroscopic nuclear moment $M$. Thus the emf is proportional to $\omega M$. The macroscopic nuclear moment is, in turn, proportional to the microscopic moment times the nuclear polarization. Thus, in order to correct for the additional nuclear polarization at the higher frequencies and the frequency dependence of the induced emf, one must divide the experimental echo intensities at each point along the resonance line by the square of the frequency corresponding to that point. In these studies the rf level was adjusted at each frequency such that the amplitude of the spin echo was at, or near, a maximum. By doing this we feel we have compensated for any change in rf enhancement across the line. Since the echo maximum occurred at relatively low rf levels, the signals are believed to be mainly due to nuclei in domain walls.

All measurements were made at 4.2°K in order to obtain good signal to noise ratios. The measurements were made in zero external magnetic fields.

## III. RESULTS AND DISCUSSIONS

### A. Experimental Results

The resulting corrected line shapes for the three systems studied are shown in Figs. 1, 2, and 3. In the higher concentration alloys the lines could not be completely traced out because of the smaller signal-to-noise ratios. It should be pointed out that the $^{51}$V nuclear

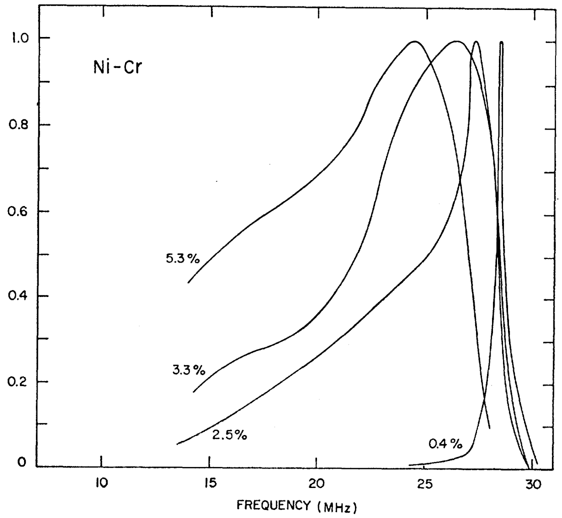

FIG. 1. The $^{61}$Ni line shapes at 4.2°K in the Ni-Cr system. The line shapes have been corrected as explained in the text.

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[2] V. Marian, Ann. Phys. (Paris) **7**, 459 (1937).

[3] C. Sadron, Ann. Phys. (Paris) **17**, 371 (1932).

[4] H. C. Van Elst *et al.*, Physica **28**, 1297 (1962).

[5] G. G. Low and M. F. Collins, J. Appl. Phys., **34**, 1195 (1963).

[6] M. F. Collins and G. G. Low, Proc. Phys. Soc. (London) **86**, 535 (1965).

resonance appears at around 8 MHz in the Ni-V alloys.[7] This resonance is very broad and overlaps the lower portion of the $^{61}$Ni resonance in the higher concentrations. However, the $^{61}$Ni spin-echo amplitude is maximum at a much lower rf level than the $^{51}$V spin-echo amplitude and thus can be experimentally separated from the $^{51}$V resonance by using a low rf level during the measurement.

### B. General Discussion

In trying to understand the behavior of the hyperfine fields in these alloys with changing solute concentration, it is of interest to consider the results found in Ref. 1 for Ni-Co alloys. As discussed in that reference, the hyperfine fields could be considered to arise from contributions from the local moments on the atoms and contributions from the average moments of the alloys.

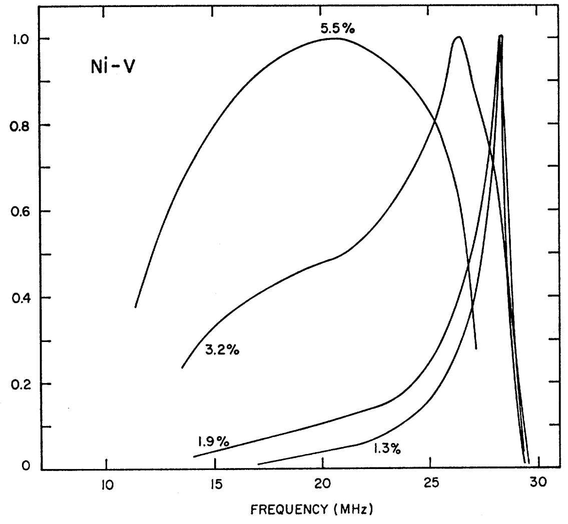

FIG. 2. Corrected $^{61}$Ni line shapes at 4.2°K in the Ni-V system.

From Eq. (1) of Ref. 1 we have

$$\bar{H}_A(c)=a\bar{\mu}_A(c)+b\bar{\mu}(c)\,. \tag{1}$$

Here $\bar{H}_A(c)$ is the average hyperfine field at the nucleus of atom $A$ in the alloy, $\bar{\mu}_A$ is the average moment of atom $A$ and $\bar{\mu}(c)$ is the average moment of the alloy. The moments $\mu$ are measured in Bohr magnetons $\mu_B$ and the fields are measured in teslas (one tesla equals $10^4$ gauss). For the case of Ni we have

$$\bar{H}_{\mathrm{Ni}}(c)=a\bar{\mu}_{\mathrm{Ni}}(c)+b\bar{\mu}(c)\,, \tag{2}$$

where in the alloy of Ni with element $x$

$$\bar{\mu}=(1-c)\bar{\mu}_{\mathrm{Ni}}(c)+c\bar{\mu}_x\,, \tag{3}$$

where $c$ is the fractional solute concentration.

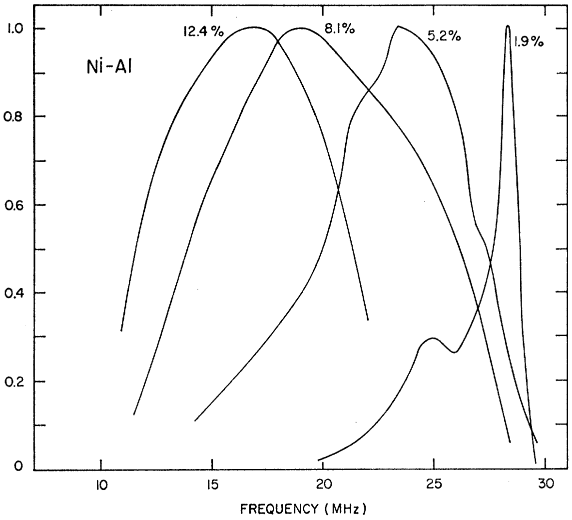

FIG. 3. Corrected $^{61}$Ni line shapes at 4.2°K in the Ni-Al system.

Since in the Ni-Co alloys $\bar{\mu}_{\mathrm{Ni}}$ is known from neutron diffraction work to have a moment of $0.6\mu_B$, independent of concentration, the value of $b$ can be determined from the change in $\bar{H}_{\mathrm{Ni}}(c)$ with concentration. Assuming the quantities $a$ and $b$ to be constants, we have from Eq. (2)

$$d\bar{H}_{\mathrm{Ni}}(c)/dc=bd\bar{\mu}(c)/dc\,. \tag{4}$$

Using $d(-\bar{H}_{\mathrm{Ni}}(c))/dc\approx 4.8T$ [from the slope of the curve of Figure (5) Ref. (1) near the Ni-rich end], and $d\bar{\mu}/dc=1.2\ \mu_B$ for Ni-Co, we obtain $b=-4.0\ T/\mu_B$.

Using the fact that $H_{\mathrm{Ni}}(0)=-7.5T$, we have then for the Ni hyperfine field near the Ni-rich end of the Ni-Co alloy system

$$\bar{H}_{\mathrm{Ni}}(c)=-8.5\bar{\mu}_{\mathrm{Ni}}-4.0\bar{\mu}(c)\,. \tag{5}$$

The above method of obtaining the constants $a$ and $b$ is different from that used in Ref. (1), where an attempt was made to fit Eq. (1) over the whole Ni-Co system. We believe the present method is more correct. First, the value of $d(-\bar{H}_{\mathrm{Ni}}(c))/dc$ used to obtain $b$ is consistent with a detailed analysis of the Ni-Co-resonance spectra.[8] Second, the values of $a$ and $b$ in Eq. (5) appear quite reasonable in that the equation predicts approximately the values of hyperfine fields for various transition elements in Ni as can be seen by an examination of Table I.

We might expect a similar equation to (5) to hold for alloys of V, Cr, and Al. Thus it is of interest to plot the quantities $\bar{H}_{\mathrm{Ni}}$, $\bar{\mu}_{\mathrm{Ni}}$ and $\bar{\mu}$ as functions of concentration of the solute atom. In the case of the alloys of Ni with V, Cr, and Al the Ni moments $\bar{\mu}_{\mathrm{Ni}}$ as well as $\bar{\mu}$ vary with concentration. We can obtain $\bar{\mu}$ directly from the net magnetization measurements. If we know $\bar{\mu}$ and the

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[7] K. Asayama *et al.*, J. Phys. Soc. Japan **19**, 1984 (1964).

[8] M. B. Stearns has proposed an interpretation of the $^{59}$Co resonance spectra at low concentrations of Co in Ni which differs from that proposed in Ref. (1). [See note added in proof to Ref. (1).] A similar interpretation of the $^{61}$Ni spectra would be consistent with a value of $d(-\bar{H}_{\mathrm{Ni}}(c))/dc$ of approximately $4.8T$. A fuller discussion of the $^{59}$Co and $^{61}$Ni resonances in Ni–Co alloys will be presented in a paper by R. L. Streever (to be published).

TABLE I. A comparison of the hyperfine fields[a] $H$ at nuclei of various solute atoms in nickel with the values predicted by Eq. (5). The local atomic moments[b] in units of the Bohr magneton $\mu_B$ are also given.

| Solute | $\mu_A(\mu_B)$ | $H$[Eq. (5)] $(T)$ | $H$(experiment) $(T)$ |
|---|---|---|---|
| Cu | 0.0 | −2.4 | −4.7 |
| Ni | 0.6 | −7.5 | −7.5 |
| Co | 1.7 | −16.9 | −12.0 |
| Fe | 2.8 | −26.2 | −28.3 |
| Mn | 3.2 | −29.6 | −32.5 |

[a] The hyperfine field values are taken from the table of M. Kontani *et al.*, J. Phys. Soc. Japan, **20**, 1737 (1965). We have assumed the field for Fe in Ni is negative.

[b] The Cu moment has been assumed to be zero. For the Ni and Co moments see M. F. Collins and D. A. Wheeler, Proc. Phys. Soc., **82**, 633 (1963). For the Fe moment see Ref. 6. The Mn moment value is consistent with $d\bar{\mu}/dc=2.4\mu_B$ and for Ni-Mn alloys (see Ref. 3).

moments on the solute atoms, we can then calculate $\bar{\mu}_{\mathrm{Ni}}$ by using Eq. (3), which can be rewritten in the following form

$$\bar{\mu}_{\mathrm{Ni}}(c)=(\bar{\mu}(c)-c\bar{\mu}_x(c))/(1-c). \qquad (6)$$

From a neutron-diffraction study, Low and Collins[6] have estimated Cr and V moments in Ni alloys. They find for small $c$, $\bar{\mu}_{\mathrm{Cr}}=(0.6\pm1.1)\mu_B$, $\bar{\mu}_{\mathrm{V}}(-1.4\pm0.4)\mu_B$. For Ni-V and Ni-Al we have used Eq. (6)and experimental values of $\bar{\mu}$ to obtain $\bar{\mu}_{\mathrm{Ni}}$ using $\bar{\mu}_{\mathrm{V}}=-1.4\mu_B$, $\bar{\mu}_{\mathrm{Al}}=0$. For the case of Ni-Cr, assuming $\bar{\mu}_{\mathrm{Cr}}=0.6\mu_B$, the difference between $\bar{\mu}_{\mathrm{Ni}}$ and $\bar{\mu}$ will be small [zero if we assume $\bar{\mu}_{\mathrm{Ni}}(c)=\bar{\mu}_{\mathrm{Cr}}(c)$] and we have not calculated $\bar{\mu}_{\mathrm{Ni}}$. In Fig. 4 we have plotted normalized values of $\bar{H}_{\mathrm{Ni}}(c)$ and $\bar{\mu}(c)$ for the three systems and also $\bar{\mu}_{\mathrm{Ni}}(c)$ for the Ni-V and Ni-Al systems. $\bar{H}_{\mathrm{Ni}}$ was obtained from the centers of gravity of the resonance curves at each concentration. The values for the average magnetic moment $\bar{\mu}$ for the three systems were determined by Marian[2] from saturation magnetization studies. However, recent measurements of the saturation magnetization for the Ni-Cr system by Van Elst have disagreed with the values previously determined by Marian[2] and Sadron[3]. Van Elst's measurements are also included in Fig. 4. For Ni-V and Ni-Al, $\bar{H}_{\mathrm{Ni}}$ lies closer to $\bar{\mu}_{\mathrm{Ni}}$ than to $\bar{\mu}$. For the Ni-Cr system, the $\bar{\mu}$ values as determined by Marian lie closer to the $\bar{H}_{\mathrm{Ni}}$ values than do the $\bar{\mu}$ values of Van Elst.

### C. Detailed Discussion

In order to obtain a more detailed understanding of the nuclear resonance spectra we now consider the magnetic disturbance around the solute atoms in these alloys. In addition to estimating the value of the solute atom moments in Ni-V and Ni-Cr alloys, Collins and Low also obtain information regarding the magnetic moment distribution on Ni atoms neighboring the solute atom. If the magnetic disturbance is limited primarily to these atoms as the results of Collins and Low suggest, then the Ni atoms near the solute atom in Ni-Cr and Ni-V must experience appreciable reductions in their magnetic moments in order to account for the marked decrease in the magnetization in these alloys. It is particularly interesting to try to correlate the hyperfine field on an atom which is nearest neighbor to a solute atom with the magnetic moment on this atom.

In Fig. 8 of Ref. 6 Collins and Low give plots of the decrease in magnetic moment on those Ni atoms which neighbor the solute atom as a function of distance from the solute atom. We can use their data together with the value of $d\bar{\mu}/dc$ obtained from saturation magnetization studies to estimate the magnetic moments on Ni atoms in various neighbor shells from the solute atom.

Let $\mu_1$, $\mu_2$, etc. be the moments on Ni atoms in various neighbor shells from the solute atom. Let $\mu_0$ be the pure Ni moment and $\mu_x$ be the solute moment. At low concentrations, the rate of decrease of magnetization with solute concentration can be expressed by

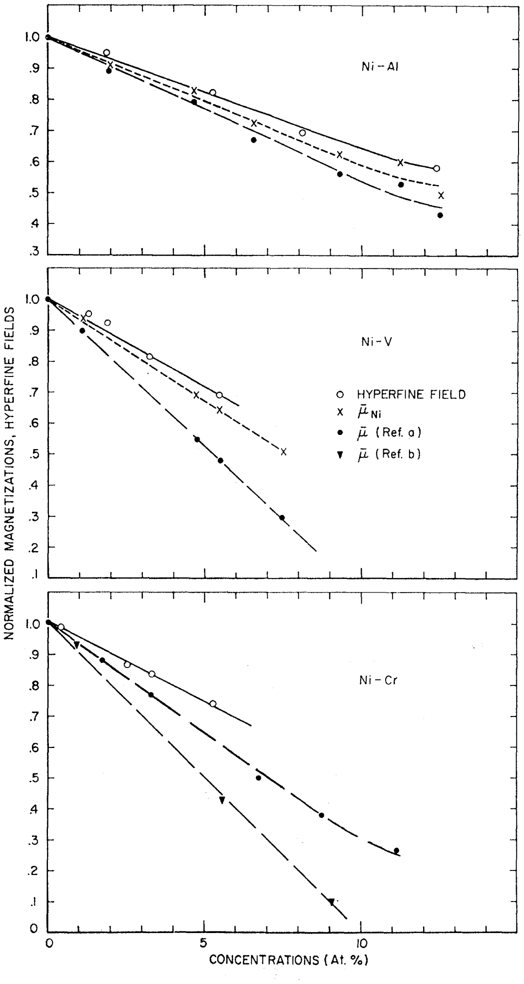

FIG. 4. The centers of gravity of the average hyperfine field $\bar{H}_{\mathrm{Ni}}$, the average magnetic moments $\bar{\mu}$, and calculated values of the average nickel moment $\bar{\mu}_{\mathrm{Ni}}$ are plotted as a function of concentration. All quantities are normalized to unity in pure nickel. (a) Ref. 2 and (b) Ref. 4.

the following equation,

$$d\bar{\mu}/dc=(\mu_x-\mu_0)-\sum_\alpha N_\alpha\Delta\mu_\alpha\,, \qquad (7)$$

where $N_\alpha$ is the number of neighbors in the $\alpha$th shell surrounding the solute atom and $\Delta\mu_\alpha$ is the decrease in moment for Ni atoms in shell $\alpha$ from the value 0.6 $\mu_B$. The $\Delta\mu_\alpha$'s are positive quantities.

In Table II we tabulate for Ni-Cr the values of $\Delta\mu_\alpha/\Delta\mu_1$ (the ratio of the decrease in moment of Ni atoms in shell $\alpha$ to the decrease in moment of Ni atoms in the nearest-neighbor shell to the solute atom) obtained from Fig. 8 of Ref. 6. We also tabulate $N_\alpha$ and $r_\alpha$ the neighbor distances and shell radii. Let us use Eq. (7) to calculate $\Delta\mu_1$ for the case of Ni-Cr. We use $\mu_x=\mu_0=0.6\mu_B$ and values of $\Delta\mu_\alpha/\Delta\mu_1$ from Table II. Using Marian's value of $d\bar{\mu}/dc=-4.5\mu_B$, we obtain $\Delta\mu_1=0.15\mu_B$. Using Van Elst's value of $d\bar{\mu}/dc=-6.0\mu_B$, we find $\Delta\mu_1=0.20\mu_B$. Thus we see that $\Delta\mu_1$ should be $\approx 0.2\mu_B$ and $\mu_1\approx 0.4\mu_B$.

Consider now the hyperfine field at the nucleus of an atom which is nearest neighbor to a solute atom. As discussed in Ref. 1, the first term in Eq. (1) represents the contribution to the hyperfine field from the moment on the parent atom while the second term represents the contribution from neighboring atoms. Taking into consideration the change in moment on the Ni atom which is nearest neighbor to the solute atom but assuming the quantity $a$ has the value given in Eq. (5), we can write the field $H_1$ at the nucleus of an atom which is nearest neighbor to a solute atom approximately as

$$H_1=-8.5\mu_1-B_1\,. \qquad (8)$$

Here, as in Eq. (5), the first term represents the contribution from the parent atom, $\mu_1$ is now the moment on atoms which are nearest neighbors to the solute atom and $B_1$ represents the contribution to $H_1$ from neighboring atoms. Consider the neighbor environment of a Ni atom which is the nearest neighbor to the solute atom. Atoms in various neighbor shells to this Ni atom will have their moments reduced by virtue of the fact that they are themselves nearest, next-nearest, etc. neighbors to the solute atom. Thus $B_1$ should have a value generally somewhat less than the corresponding term in pure Ni which from Eq. (5) is $4.0\mu_0$ or 2.4 $T$.

Consider the case of Ni-Cr. From the first term alone in Eq. (8) we expect a decrease in the absolute value of the hyperfine field for a Ni atom which is nearest neighbor to a solute atom from the value in pure Ni by an amount 8.5 $\Delta\mu_1$ or $\approx 1.7T$ (using $\Delta\mu_1=0.2\mu_B$). This corresponds to a frequency shift of $-6.5$ MHz from the pure Ni frequency. Consider now the second term in Eq. (8). In order to estimate $B_1$ we must consider the neighbor environment of a Ni atom which is nearest neighbor to an isolated solute atom such as Cr. We can obtain for this Ni atom the number of Ni atoms in its various neighbor shells which are nearest neighbors, next-nearest neighbors, etc. to the solute atom.[9] The results are summarized in Table III where $N_{\alpha m}$ is the number of atoms in the $\alpha$th neighbor shell of the Ni in question which are also $m$th nearest neighbors to the solute atom. In the case of Ni-Cr we assume that the Cr atom itself has a moment $0.6\mu_B$. Then the total moment reduction for Ni atoms in the nearest-neighbor shell to a Ni atom which is itself a nearest neighbor to the Cr will be given by the following equation

TABLE II. The values of the shell radii $r_\alpha$ for the $\alpha$th-neighbor shell, the number of neighbors in the $\alpha$th shell $N_\alpha$, and the ratio of the decrease in moment of Ni atoms in shell $\alpha$ to the decrease in moment of Ni atoms in the nearest-neighbor shell ($\Delta\mu_\alpha/\Delta\mu_1$) are tabulated. The values of $\Delta\mu_\alpha/\Delta\mu_1$ are taken from Fig. 8 of Ref. 6.

| $\alpha$ | Distance $r_\alpha$(Å) | $N_\alpha$ | $\Delta\mu_\alpha/\Delta\mu_1$ |
|---|---|---|---|
| 1 | 2.5 | 12 | 1.00 |
| 2 | 3.5 | 6 | 0.62 |
| 3 | 4.3 | 24 | 0.37 |
| 4 | 5.0 | 12 | 0.19 |
| 5 | 5.6 | 24 | 0.13 |
| 6 | 6.1 | 8 | 0.06 |

TABLE III. Neighbor environment of a nickel atom which is nearest neighbor to an isolated solute atom. $N_{\alpha m}$ is the number of atoms in the $\alpha$th-neighbor shell to the nickel which are $m$th nearest neighbors to the solute atom.

| $\alpha$ | $N_{\alpha 1}$ | $N_{\alpha 2}$ | $N_{\alpha 3}$ | $N_{\alpha 4}$ | $N_{\alpha 5}$ |
|---|---|---|---|---|---|
| 1 | 4 | 2 | 4 | 1 | 0 |
| 2 | 2 | 0 | 2 | 0 | 2 |

$$\sum_m N_{1m}\Delta\mu_m=4\Delta\mu_1+2\Delta\mu_2+4\Delta\mu_3+\Delta\mu_4\,. \qquad (9)$$

Using Table II and $\Delta\mu_1=0.2\mu_B$, this sum is just $1.4\mu_B$ or 19% of the total pure Ni moment value for this shell of $12\mu_0$ of $7.2\mu_B$. Similarly, for the second shell of neighbors we find a total moment reduction given by the following equation:

$$\sum_m N_{2m}\Delta\mu_m=2\Delta\mu_1+2\Delta\mu_3+2\Delta\mu_5\,. \qquad (10)$$

This sum is just $0.6\mu_B$ or 17% of the total pure Ni moment value for this shell of $6\mu_0$ or $3.6\mu_B$. Consequently, if we assume $B_1$ to arise primarily from atoms in the first two neighbor shells, to a good approximation we can assume it to be reduced by about 18% from the neighbor contribution in pure Ni. Since in pure Ni this contribution from Eq. (5) is $4.0\mu_0$ or $2.4T$, the reduction will be about $0.4T$. Consequently, the total reduction in the absolute value of the hyperfine field, from the pure Ni, associated with both terms in Eq. (8) will be $1.7T+0.4T$ or $2.1T$, corresponding to a frequency shift for Ni atoms which are nearest neighbors to the Cr atom of $-8.0$ MHz from the pure Ni frequency.

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[9] This method is similar to that used by S. Kobayashi *et al.* [J. Phys. Soc. Japan 21, 65 (1966)] in analyzing their results for Co-based alloys. However, they consider the nieghbor contribution to be due solely to the effects of nearest neighbors while we consider the effects of more distant neighbors. Also, the relative contributions to the hyperfine field from the parent and neighboring atoms, which are used in the present paper, are different from those used by Kobayashi *et al.*

Now consider the experimental spectra for the Ni-Cr alloys. The broad knee at about 17.5 MHz has about the right integrated intensity to be associated with Ni atoms which are nearest neighbors to the Cr atom. (At 3% the number of Ni atoms which are nearest neighbors to the Cr atom, independent of the number of Cr atoms in their more distant neighbor shells, should be statistically 25.8%.) Structure closer in to the pure Ni line at 28.5 MHz is then assumed to be associated with Ni atoms in more-distant-neighbor shells from the Cr atom. Thus we believe that the knee at 17.5 MHz in the 3.3% Ni-Cr sample represents the effect of Ni atoms with one Cr atom in the first neighbor shell and various other configurations in the more-distant-neighbor shells. Similarly, we believe that the peak at 26.5 MHz in the 3.3% Ni-Cr sample represents the effect of Ni atoms with no Cr atoms in the first-neighbor shell and various other configurations in the more distant shells. Thus the frequency shift between the knee and the peak of the 3.3% Ni-Cr spectra probably gives an estimate of the field shift due to one Cr atom in the nearest neighbor to a Ni atom. This shift is about −9 MHz, which is in reasonably good agreement with the value estimated above based on Eq. (8).

We have just assumed that the main peak in the 3.3% Ni-Cr sample represents the effect of Ni atoms with no Cr atoms in the first-neighbor shell and various other configurations in more distant shells. From statistical considerations one can show that the shift of the main peak of the 3.3% Ni-Cr spectra should give a rough estimate of the frequency shift for Ni atoms with one Cr atom in the third neighbor shell. This is ≈2 MHz or $0.53T$. In analogy to Eq. (8), we can write for the field at a Ni atom which is a third neighbor to a Cr atom

$$H_3=-8.5\mu_3-B_3. \tag{11}$$

Considering the first term of Eq. (11), the $0.53T$ shift corresponds to a $\Delta\mu_3$ of about $0.06\mu_B$. This is about 30% of $\Delta\mu_1$, in good agreement with Collins and Low (see Table I).

Let us now turn to the case of the Ni-V alloys. The results of Low and Collins indicate that the magnetic disturbance around the solute atom will be more widespread than in the Ni-Cr case. Although at low concentrations the Ni-V and Ni-Cr curves are qualitatively similar, the shift of the peak of the 5.5% Ni-V curve is considerably greater than for the 5.3% Ni-Cr curve and the structure is less resolved in Ni-V. This seems to indicate that the shift at the second-neighbor shell may be more nearly comparable to that at the first-neighbor shell to the solute atom. Thus (in agreement with Low and Collins) a somewhat more widespread disturbance may be present in the Ni-V system.

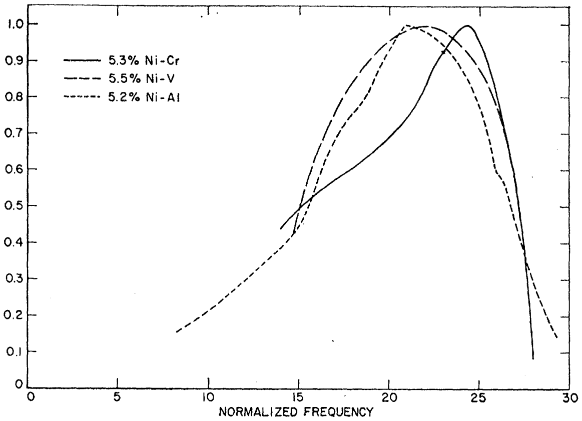

FIG. 5. The line shapes normalized to constant $d\bar{\mu}/dc$ are shown for the three systems for concentrations near 5%.

Now consider the Ni-Al alloys results. For Ni-Al, $d\bar{\mu}/dc$ is $-3\mu_B$ compared with a value of $-4.5\mu_B$ in Ni-Cr and $-5.5\mu_B$ in Ni-V (Marian), so we expect a smaller disturbance due to the Al solute atom, as is observed. If we assume the magnetic disturbance is confined to those Ni atoms which are nearest neighbors to the Al atom and that $\mu_{\rm Al}=0$, we obtain from Eq. (7) that $\Delta\mu_1=0.2\mu_B$ or $\mu_1=0.4\mu_B$. If, however, we assume that the magnetic disturbance is as least as widespread as in the Ni-Cr case then we can estimate $\Delta\mu_1$ for Ni-Al to be 3/4.5 times $\Delta\mu_1$ for Ni-Cr or about 0.1 $\mu_B$.

The line at 25 MHz in the 1.9% Ni-Al spectra, shifted 3.5 MHz from the pure Ni line, has about the right integrated intensity to be associated with Ni atoms which are nearest neighbors to the Al. Using $\Delta\mu_1=0.1\mu_B$ for Ni-Al, from the first term in Eq. (8) we expect a decrease in the absolute value of the hyperfine field of $0.85T$ from the pure Ni value corresponding to a frequency decrease of 3.2 MHz, which is approximately equal to the observed value.

The possibility also exists that the $^{27}$Al nuclear resonance may occur near the $^{61}$Ni resonance in the Ni-Al alloys. Thus at least part of the structure in the Ni-Al alloys could be due to the $^{27}$Al resonance. However, from the results of Asayama *et al.*,[7] who have studied the $^{27}$Al nuclear resonance in Fe and Co, one might expect that the $^{27}$Al nuclear resonance in Ni should come at a lower frequency.

In considering the spatial variation of the magnetization or the hyperfine field shifts, it is the disturbance at various neighbor shells relative to each other rather than the total disturbance $d\bar{\mu}/dc$ that is of interest. That is, multiplying the disturbance at each neighbor shell away from the solute atom by the same amount does not change the ratio of the disturbance at one shell relative to the next. Consequently, to obtain an idea of the delocalization of the magnetic disturbance from the resonance spectra, we should normalize them to the same $d\bar{\mu}/dc$. (Since as we have seen $\bar{H}$ is approximately proportional to $\bar{\mu}$, normalizing the spectra to the same $d\bar{\mu}/dc$ at any concentration is approximately equivalent to normalizing to the same center of gravity.) We have done this in Fig. 5. We have taken $d\bar{\mu}/dc = -3\mu_B$, $-4.5\mu_B$, and $-5.5\mu_B$ for Ni-Al, Ni-Cr and Ni-V, respectively. The 5.3% Ni-Cr has been plotted directly. We have then plotted the 5.5%-Ni-V and 5.2%-Ni-Al spectra by first expanding the frequency scale around 28.5 MHz by 4.5/3 in the Al case and contracting it by 4.5/5.5 in the V case. The resulting curves enable a comparison of the Ni-Cr, Ni-V, and Ni-Al results, all about 5%, normalized to the same $d\bar{\mu}/dc$. In the Ni-Cr case there is a fairly pronounced knee which we have related to Ni atoms in the nearest-neighbor shell to the solute atom, while the main peak was related to Ni atoms in more distant shells. The fact that in the Ni-Al and Ni-V cases the peak of the curve is shifted over relative to the knee or to the center of gravity means that the magnetic disturbance in more distant shells is more comparable to the disturbance in the nearest neighbor shells in these two systems. A similar scaling, using Van Elst's value of $d\bar{\mu}/dc = -6\mu_B$ for Ni-Cr, gave a very poor fit of the Ni-Cr with the Ni-Al and Ni-V curves, indicating that, at least for our samples, the data of Marian or Sadron are more applicable.

## IV. CONCLUSION

As in the case of the Ni-Co system previously studied it has been found that the hyperfine field at the site of Ni nuclei in Ni-V, Ni-Cr and Ni-Al systems has two contributions. The major contribution is due to the moment on the parent atom and a smaller contribution is from moments on neighboring atoms. The greater delocalization of the magnetic disturbances in these three systems is in contrast to the localized behavior of the Ni-Co system. The magnetic disturbances seem to be spatially more widespread in the Ni-Al and Ni-V systems than in the Ni-Cr system. The spatial variation of the magnetization for the Ni-Cr system, as deduced from the resonance spectra, is in agreement with results obtained by Collins and Low by means of neutron scattering techniques.

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# Relaxation Times for Metastable States in the Mean-Field Model of a Ferromagnet*

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Relaxation from metastable to stable states is considered for a mean-field model Ising ferromagnet in which each spin interacts equally with every other spin in the system. Spins are chosen at random and flipped over with probability given by a suitable Boltzmann factor. Approximate solutions to the stochastic equations, confirmed by computer calculations on small systems, indicate a relaxation time increasing exponentially with the size of the system (contrary to one's expectation for a system with short-range interactions).

## I. INTRODUCTION

THE description of metastable states on a fundamental level is both an interesting and unsolved problem in statistical mechanics. The long lifetime (especially compared with times characterizing molecular processes) observed for many such states suggests that an elementary extension of well-established procedures in the statistical mechanics of stables states might serve to cover metastable states as well.

In fact, metastable states are fairly easily defined in certain model systems of magnets or fluids with an attractive potential whose range is permitted to become infinite (the magnitude simultaneously going to zero) at some point in the calculation. Probably the simplest of these is the mean-field (molecular-field or Weiss) model of a ferromagnet. The mean-field theory is often considered an approximate method for solving the Heisenberg or Ising model with nearest-neighbor interactions.[1] It may also be regarded as the exact solution (in the limit of a large system) for a model in which each atom interacts equally with every other atom through an Ising exchange potential.[2] We shall adopt the latter point of view in this paper and investigate the following question in the case of atoms of spin-$\frac{1}{2}$: if such a ferromagnet is at some particular time in a

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[1] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Company, Philadelphia, Pennsylvania, 1966).

[2] F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill Book Company, Inc., New York, 1937), p. 153. The analogous model for a lattice gas was discussed by K. Husimi at a meeting of the Physical Society of Japan in May, 1953 (unpublished) and by H. N. V. Temperley, Proc. Phys. Soc. (London) **A67**, 233 (1954)