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**AN NMR AND NUCLEAR RELAXATION STUDY
OF SATELLITE LINES IN DILUTE
Co-Cr, Co-V, and Co-Mn ALLOYS**

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**Solid State and Low Temperature
Physics Group**

SCHOOL OF PHYSICS AND ASTRONOMY

MARCH 1971

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MINNEAPOLIS, MINNESOTA

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Work supported in part by the U.S. Atomic Energy Commission

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- * Work supported in part by the U. S. Atomic Energy
Commission under Contract No. AT(11-1) 1569.

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ACKNOWLEDGEMENTS

We would like to thank the staff of the electronics shop, the student shop, and the glass technology shop for their assistance and cooperation.

One of us, J. Aslam, would particularly like to thank:

My wife Ferre, whose encouragement was a source of great inspiration for me;

Fellow graduate students Jim Holliday and Carl Smith for occasional assistance and several helpful discussions;

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ABSTRACT

A study has been made of the distribution of hyperfine fields at cobalt nuclei in the dilute alloys of Co-Cr, Co-V, and Co-Mn using NMR techniques at 4.2 K. The spectra for Co-Cr and Co-V alloys are characterised by three satellite lines in addition to the main cobalt line. In each of these two cases, the nearest neighbor line is split into two components due to dipolar and pseudodipolar effects in the domain wall as predicted by the Murray-Marshall theory of NMR in dilute ferromagnetic alloys. The splitting gives us a pseudodipolar moment of $-(6.1 \pm 0.7)\mu_B$ for a Cr impurity in cobalt and $-(4.3 \pm 0.7)\mu_B$ for a V impurity in cobalt. The third satellite line in these systems is shown to arise from cobalt atoms in the third neighbor shell around the impurity. The location of the second neighbor line in these two alloys has been determined by drawing suitable line shapes for the three satellite lines. For Co-Mn alloy, only one clearly resolved satellite line has been observed at 209.5 MHz. The absence of any splitting in this line gives us an upper limit to the pseudodipolar moment of $-(1.9 \pm 0.7)\mu_B$.

A phenomenological model similar to that of Streever and Uriano and Kobayashi et al. has been used to predict the hyperfine field shifts corresponding to the Zeeman frequency of the various neighboring satellite lines using the magnetic moment distribution on cobalt atoms around these impurities in the light of recent neutron diffraction work of Cable and Hicks. The agreement between the observed and predicted hyperfine field shifts is quite good for Co-Cr and Co-V alloys but there

is a large discrepancy in the case of Co-Mn alloy if the satellite line is assumed to be the nearest neighbor line.

The nuclear spin-spin relaxation time T_2 has been measured for cobalt nuclei at the main line and all satellite lines in the alloys. At the main line T_2 is shorter than that in pure cobalt (30-50 μ s in the alloys, 88 μ s in pure cobalt). However, at all the satellite lines T_2 is greater than that in pure cobalt. The data are discussed in qualitative terms on the basis of the Suhl-Nakamura interaction and a pinning of domain walls caused by the presence of impurities as suggested by Stearns.

Finally an echo envelope modulation has been observed for the satellite line at 172.5 MHz in the Co-Cr alloy. The modulation period is $(5.5 \pm 0.5)\mu$ s and is shown to be of quadrupolar origin resulting from the broken symmetry of the lattice due to alloying.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	i
ABSTRACT	ii
LIST OF FIGURES	vi
<u>Chapter</u>	
1 INTRODUCTION	1
2 THEORETICAL BACKGROUND	6
2.1 The Magnetic Properties of <u>Co-Cr</u> , <u>Co-V</u> and <u>Co-Mn</u> Alloys	6
2.2 Satellite Lines in Dilute Alloys- Murray-Marshall Theory.	7
2.3 Nuclear Spin-Spin Relaxation in Ferromagnets	17
2.4 Modulation of the Spin Echo Envelope. . .	20
3 EXPERIMENTAL SET-UP AND PROCEDURES	25
3.1 Sample Preparation.	25
3.2 CW vs Pulsed Methods of NMR Detection . .	28
3.3 Tunnel Diode NMR Spectrometer	30
3.4 Spin Echo Spectrometer.	33
3.5 NMR Spectra using Spin Echo Spectrometer.	37
3.6 Measurement of Nuclear Spin-Spin Relaxation Times, T_2	39
4 RESULTS AND DISCUSSION	42
4.1 NMR Spectra	42
4.2 A Phenomenological Model for Hyperfine Fields in the Alloys	49

TABLE OF CONTENTS (cont.)

4.3	Nuclear Spin-Spin Relaxation Times	54
4.4	The Echo Envelope Modulation Effect. . . .	57
5	CONCLUSIONS	62
<u>Appendix</u>		
A	Filing Machine for NMR Samples.	64
B	Supplies for Tunnel Diode NMR Spectrometer. . . .	65
C	The Multivibrator Circuit	66
References.		67

LIST OF FIGURES

<u>Figure</u>		<u>Following Page</u>
1	Block Diagram of Tunnel Diode NMR Spectrometer. .	30
2	Tunnel Diode Oscillator Circuit	30
3	Block Diagram of Spin Echo Spectrometer	33
4	Schematic Diagram of the Tank Circuit Set-Up. . .	34
5	Co^{59} NMR Spectrum in <u>Co</u> -Cr.	42
6	Co^{59} NMR Spectrum in <u>Co</u> -V	46
7	NMR Spectrum of Co^{59} in <u>Co</u> -Mn	48
8	Echo Envelope Modulation in <u>Co</u> -Cr	57
9	A Perspective Drawing of the Filing Machine . . .	64
10	Supplies for the Tunnel Diode NMR Spectrometer. .	65
11	The Multivibrator Circuit	66

Chapter 1

Introduction

Studies of satellite lines in NMR spectra of dilute ferromagnetic alloys have been a subject of considerable interest ever since the first observation of nuclear resonance in ferromagnetic cobalt by Gossard and Portis.¹ The effect of dilute Ni and Fe impurities on the nuclear resonance of cobalt was studied by La Force *et al.*², who found that characteristic satellite lines appear on either side of the main Co line on alloying. On the basis of their intensity ratios, these satellite lines were identified as coming from Co atoms with an impurity atom in the nearest neighbor, second nearest neighbor, and third nearest neighbor positions. At approximately the same time, Koi *et al.*³ published results of similar experiments on several alloys of cobalt including two of the alloys studied in the present work. They found no clearly resolved satellite lines in alloys other than Co-Fe and Co-Ni. For these two alloys their results agreed with those of La Force *et al.*² Both of these early investigations were carried out using steady state NMR methods at room temperature. Kobayashi *et al.*⁴, using the spin echo method at 77K, were the first to detect a satellite line far away (~40MHz) from the main line (~217MHz) in both Co-V and Co-Cr systems. This line was attributed by them as being due to cobalt nuclei having an impurity atom in the nearest neighbor position. Riedi *et al.*⁵ in a recent work on Co-V alloys at 4.2K, using the spin echo technique, have

found an additional satellite line corresponding to an impurity atom in the third neighbor position with respect to the host. In our spin echo work at 4.2K we have observed one more line than Riedi *et al.*⁵ for Co-V alloy and two more lines than Kobayashi *et al.*⁴ for Co-Cr alloy.

Although experimentalists have almost always interpreted the satellite lines as coming from various neighboring shells, the theorists have come up with other ideas. Portis and Kanamori,⁶ referring to the work of La Force *et al.*,² argued that these lines were too weak in intensity to be caused by the three neighboring shells. They proposed instead that all lines were associated with the nearest neighbor shell split by the dipolar field from the magnetic moment of the impurity and a pseudo-dipolar field resulting from the anisotropic distortion of the neighboring d-shells by the charge on the impurity. Their estimated value of the frequency shift for various satellite lines is in good agreement with the observed values. From the magnitude and sign of the observed splitting, they computed the apparent moment on the impurity site which enabled them to calculate the pseudo-dipolar moment. They found that the pseudo-dipolar moment thus calculated was in agreement with that expected from the distortion of neighboring d-shells.

Murray and Marshall⁷ in a subsequent work calculated the effect of dipolar and quadrupolar interactions on the nuclear magnetic resonance line shape from a ferromagnet by taking an average over the domain wall weighted by the enhancement factor which varies through the wall. They concluded that in an f.c.c.

lattice, such as cobalt, the nearest neighbor line is split into three components, with 11/12 of the intensity going into two of these. The second neighbor line is also split into three components, with 5/6 of the intensity going into two of these. As a general rule, the third neighbor line is only asymmetrically broadened by these interactions. Two of the three alloy systems studied by us show splitting of the near neighbor line, the third one, Co-Mn shows a single, rather sharp satellite line compared with Co-V and Co-Cr. The satellite line for Co-Mn system and the splitting of near neighbor line in Co-V and Co-Cr alloys has not been reported in the literature thus far. We will analyse our data on the satellite line frequencies in the light of recent neutron diffraction study of magnetic moment distribution in these alloys by Cable and Hicks.⁸

Important as NMR satellite line work is to an understanding of the magnetic properties of such alloys, there have been few attempts at theoretical calculation of satellite line frequencies. The theorists have not even had more than moderate success in predicting hyperfine fields even in pure ferromagnetic metals.⁹ There are just too many complex and competing mechanisms involved. Kobayashi *et al.*⁴ in the case of Co alloys and Streever and Uriano¹⁰ for Co and Ni alloys have used empirical relations to estimate the hyperfine field shifts at host nuclei which are nearest neighbors to an impurity with some degree of success. We find that their empirical relation gives reasonably good agreement for all satellite line frequencies in the case of Co-Cr and Co-V alloys but a large dis-

crepancy for the Co-Mn system.

We have also studied the spin-spin relaxation of the cobalt nuclei corresponding to various peaks in the NMR spectra to obtain information on the effect of impurity on nuclear spin-spin relaxation of neighboring cobalt nuclei. In the case of the Co-Cr alloy, the echo decay envelope was found to be modulated for one of the satellite lines. No such effect has been observed for the other two alloys.

All measurements reported in this work were made using standard spin echo techniques at 4.2K. A tunnel diode cw NMR spectrometer was used for preliminary checks on the alloys after annealing.

The presentation of this work will be along the following lines: We start with a chapter on theoretical considerations involved in the present work. This involves a brief description of the magnetic properties of the dilute alloys under study. We then go on to a discussion of satellite lines and Murray-Marshall theory of the NMR spectra of dilute ferromagnetic alloys. A discussion of nuclear spin-spin relaxation in ferromagnets is next carried out with its extension to alloy systems. The chapter is concluded with a discussion of the modulation of the spin echo decay envelope.

Chapter 3 has details on sample preparation, experimental set-up for cw and pulsed NMR measurements, and how this was used to obtain data reported in this thesis.

In chapter 4 we give the results of our experiments along with a discussion in the light of background developed in chap-

ter 2.

Important conclusions of this work are summarized at the end.

Chapter II

Theoretical Background

2.1 The Magnetic Properties of Co-V, Co-Cr, and Co-Mn Alloys

In this section we like to mention briefly some of the magnetic properties of Co-V, Co-Cr, and Co-Mn alloys which are related to the present work. Pure cobalt has a saturation magnetic moment of $1.7\mu_B$ per atom. From neutron diffraction measurements this moment is known to be well localised on the individual cobalt atoms.¹¹ Saturation magnetisation measurements on Co-Cr and Co-Mn alloys show that the addition of each impurity atom causes a loss of $6.4\mu_B$ and $4.5\mu_B$ respectively.¹² For the Co-V alloy system magnetisation measurements have not been reported but Lomer and Marshall¹³ calculate it to be $(6.0 \pm 0.3)\mu_B$ from the electronic structure of Co and V expected in the alloy. Recently, Cable and Hicks⁸ have determined this value to be $(6.8 \pm 1.3)\mu_B$ on the basis of their neutron diffraction work on this alloy. This is in agreement with the above predicted value of Lomer and Marshall.¹³ In view of the large inherent error in neutron diffraction measurements and the excellent agreement between the observed and calculated values for Fe-V and Ni-V alloys, we will use the above calculated value for the Co-V alloy for our calculations.

For all the alloy systems studied in this work, the loss of moment is much larger than could be accounted for by the host-impurity moment difference. Low and Collins,¹⁴ as a result of their neutron scattering experiments on dilute nickel alloys

with transition metal impurities, concluded that for alloys which lie on the Slater-Pauling curve¹⁵ (e.g., Co-Ni), the magnetic moment disturbance due to the impurity is localised at the impurity itself and the host atom moments remain unaltered. On the other hand, for alloys which deviate from the Slater-Pauling curve, there is a widespread magnetic moment disturbance leading to considerable loss of moment at host atoms in several shells around the impurity. The alloys studied in this work deviate sharply from the Slater-Pauling curve and neutron scattering experiments on these by Cable and Hicks⁸ showed that a negative magnetic moment disturbance (resulting in loss of moment at cobalt atoms) extends out to $\sim 5\text{\AA}$ (fourth neighbor). However, within the limits of their experimental error, they were able to fit their data to the theoretical expression for differential cross section for neutron scattering due to Marshall¹⁶ using only parameters for host-impurity moment difference and magnetic moment disturbance at the first and second neighbor shells around the impurity. We will use these magnetic moment disturbance parameters and the impurity magnetic moments derived in their work in estimating the hyperfine field shifts at cobalt nuclei in certain neighborhood of the impurity in a phenomenological model. The predictions of this model will finally be compared with the observed values.

2.2 Satellite Lines in Dilute Alloys - Murray-Marshall Theory

When an impurity atom is introduced in a ferromagnetic metal, the impurity atom will generally acquire a net charge which

will be screened off by electrons on the surrounding atoms. The distortion of electron clouds of the neighbors changes the contact field at the host nuclei. This change in the contact field depends only on the distance of the host nucleus from the impurity.² Thus one would expect to observe different hyperfine fields at host nuclei located at different neighbor positions with respect to the impurity. These will manifest as characteristic satellite lines in the NMR spectra of such alloys. Of course, for some far neighbors of the impurity the satellite lines may not be resolved from the main line leading to a broadening of the main line. Furthermore, the satellite lines due to nearest neighbors and second nearest neighbors may be split into components due to anisotropic interactions like the dipolar, pseudo-dipolar, and quadrupolar interactions.

Murray and Marshall⁷ have studied the effect of the aforementioned anisotropic interactions on the NMR line shape of the host nuclei in dilute ferromagnetic alloys. In what follows we give a brief outline of their theory leading to the predictions relevant to this work.

It has been shown by Weger et al.¹⁷ that for low rf power pulses the nuclear spin echo signal comes from nuclei in the domain walls. Since the direction of local magnetisation varies continuously in going through the wall, the observed signal should be an average over all the nuclei in the wall. Let $q(\phi)$ denote the strength of the nuclear resonance signal coming from nuclei located in that part of the wall where the local magnetisation makes an angle ϕ with the direction of easy axis and $\Delta(\omega - \Omega)$

the line shape in the absence of any broadening from the wall (Ω containing the part of interaction energy which is independent of ϕ); then the power absorbed at frequency ω in the presence of an anisotropic interaction $g(\phi)$ is given by

$$P(\omega) = \int_0^{\phi_0} q(\phi) \Delta(\omega - \Omega - g(\phi)) d\phi,$$

the domain wall being assumed to be a ϕ_0 degree wall. For convenience of calculation $\Delta(\omega - \Omega - g(\phi))$ is replaced by $\delta(\omega - \Omega - g(\phi))$, the effects of finite line-width shall be considered at the end. They next show that the signal strength $q(\phi)$ is related to the magnetic anisotropy energy by the relation,

$$q(\phi) = \{f(\phi)\}^{1/2}$$

and for face-centered cubic cobalt, in which the direction of easy magnetisation is along $[1\ 1\ 1]$, the anisotropy energy is given by

$$\begin{aligned} f(\phi) = & \frac{3}{4} K_1 \sin^2 \phi \cos^2(\phi + \alpha) \\ & + \frac{2K_2}{6^3} \sin^2 \phi (2 - \cos^2 \phi + 23 \cos^4 \phi + 10\sqrt{2} \cos^2 \phi \sin \phi \\ & - 6\sqrt{2} \cos \phi \sin \phi) \end{aligned} \quad (1)$$

where $\cos 2\alpha = \frac{7}{9}$; $\sin 2\alpha = \frac{4}{9} \sqrt{2}$.

Thus,

$$P(\omega) = \int_0^{\phi_0} \{f(\phi)\}^{1/2} \delta(\omega - \Omega - g(\phi)) d\phi \quad (2)$$

where $f(\phi)$ is given by the above expression.

To be considered next are the anisotropic interactions, i.e., the dipolar, the pseudo-dipolar and the quadrupolar interactions.

a) Dipolar interaction - If the magnetic moment on the impurity differs from that of the host by μ_d , it will produce a dipolar field on its own neighbors when the host magnetic moments are undisturbed to first approximation. The dipolar field at a distance $\underline{R}$ from an impurity is given by

$$\frac{\mu_d}{|\underline{R}|^3} (3 \cos^2 \theta - 1)$$

where $\cos \theta = \hat{\underline{R}} \cdot \hat{\underline{I}}(\phi)$ and $\hat{\underline{I}}(\phi)$ is the direction of local magnetisation. The above formula is strictly true only for alloys that lie on the Slater-Pauling curve. For alloys that do not lie on the Slater-Pauling curve, the magnetic moment disturbance due to the impurity extends out to several neighbors and the effect of loss of moment on atoms in the neighborhood of the impurity gives rise to a further contribution to the dipolar field which must be considered also. Since in the case of cobalt alloys this represents a small perturbation, its effect will be considered after contributions from other more important sources have been completely accounted for.

b) Pseudo-dipolar effect - When the d shells of the host atoms distort to shield out the impurity charge, the redistribution of the spin density produces a magnetic field at the nucleus. This field can be expanded in spherical harmonics and to first order can be considered as a dipolar field (hence its name).

It can be written as

$$\frac{\mu_p}{|\underline{R}|^3} (3 \cos^2 \theta - 1)$$

where again $\cos \theta = \hat{R} \cdot \hat{I}(\phi)$. Unlike the true dipolar field, the pseudo-dipolar field cannot easily be calculated in any simple situation; so when the total dipolar moment μ_{tot} which appears on the impurity is found from experiment, the pseudo-dipolar moment is given by

$$\mu_p = (\mu_{\text{tot}} - \mu_d)$$

Thus we can see that the field due to the distortion of the d shells of the host atom is given in terms of a dipole moment which would cause the same magnetic field as if it were on the impurity site. It follows that, unless this interaction falls off as $1/R^3$, μ_p will be a function of $\underline{R}$ and so will take on a different value for each shell of neighbors.

c) Quadrupole effects - The impurity charge will produce an electric field gradient at the host nuclei; it is not easily possible to calculate its magnitude as complex shielding and antishielding effects occur.¹⁸

The quadrupole interaction is given by

$$v_m^{(1)} = v_Q (m-1/2) (3 \cos^2 \theta - 1)$$

where $\cos \theta = \hat{H} \cdot \hat{c} = \hat{I}(\phi) \cdot \hat{R}$.

Combining the effects of all these three anisotropic interactions, we get for the total line shape,

$$\Delta(\omega - \Omega - g(\phi)) = \Delta(\omega - \Omega_R - \{\gamma \frac{\mu_d + \mu_p}{|R|^3} + \nu_Q(m-1/2)\} (3 \cos^2 \theta - 1))$$

where Ω_R is the frequency from unperturbed field plus the change in contact field due to impurity, which is a function of R .

Then putting

$$\lambda = \gamma \frac{(\mu_d + \mu_p)}{|R|^3} + \nu_Q(m-1/2)$$

and substituting it in eqn. 2, we get for fixed R

$$P_R(\omega) = \int_0^{\phi_0} \{f(\phi)\}^{1/2} \delta(\omega - \Omega_R - \lambda(3 \cos^2 \theta - 1)) d\phi, \quad (3)$$

where $\cos \theta = \hat{I}(\phi) \cdot \hat{R}$.

For face-centered cubic cobalt the easy direction is $[111]$ and other equivalent directions. Then a general direction of magnetisation $\hat{I}(\phi)$ in the domain wall has its direction cosines given by

$$\hat{I}(\phi) = \frac{1}{\sqrt{6}} [\sqrt{2} \cos \phi + \sin \phi; \sqrt{2} \cos \phi - 2 \sin \phi; \sqrt{2} \cos \phi + \sin \phi] \quad (4)$$

Further, the function $\{f(\phi)\}^{1/2}$ is only weakly dependent on K_2 in the case of cobalt. If we neglect the K_2 term in the expression for $f(\phi)$, the integral for line shapes (equation 3) can be performed analytically for all the neighboring sites. In this work we will only consider nearest neighbor lines as our experiments did not reveal any interesting feature in the other satellites observed. The positions of nearest neighbor sites are given by

$$\underline{R} = \frac{+}{-} \frac{a}{2} (1, 0, 1), \frac{+}{-} \frac{a}{2} (\bar{1}, 0, 1), \frac{+}{-} \frac{a}{2} (1, \bar{1}, 0), \frac{+}{-} \frac{a}{2} (0, \bar{1}, 1), \\ \frac{+}{-} \frac{a}{2} (1, 1, 0), \frac{+}{-} \frac{a}{2} (0, 1, 1)$$

As an illustration of the general method of evaluating the integral for $P_{\underline{R}}(\omega)$, we evaluate it for some of the sites. We write,

$$P_{\underline{R}}(\omega) = \int_0^\phi \frac{\sqrt{3K_1}}{2} \sin\phi \cos(\phi+\alpha) \delta(\omega - \Omega_R - \lambda(3 \cos^2 \theta - 1)) d\phi,$$

where $\{f(\phi)\}^{1/2} = \frac{\sqrt{3K_1}}{2} \sin\phi \cos(\phi+\alpha)$, the term involving K_2 being neglected. Let us first consider sites $\frac{+}{-} \frac{a}{2} (1, 0, \bar{1})$.

From the symmetry of $\hat{I}(\phi)$ it is clear that $\cos \theta = 0$. Thus we have

$$P_{\frac{+}{-} \frac{a}{2} (1, 0, \bar{1})}(\omega) = \int_0^\phi \frac{\sqrt{3K_1}}{2} \sin\phi \cos(\phi+\alpha) \delta(\omega - \Omega_R + \lambda) d\phi$$

This is clearly peaked at

$$(\omega - \Omega_R) = -\lambda.$$

So these two sites will give us a δ -function line shape at

$\omega = (\Omega_R - \lambda)$. Next we consider the sites $\frac{+}{-} \frac{a}{2} (1, \bar{1}, 0)$ and $\frac{+}{-} \frac{a}{2} (0, \bar{1}, 1)$. We have in this case,

$$\cos \theta = \frac{1}{\sqrt{12}} \{3 \sin \phi\} = \frac{\sqrt{3}}{2} \sin \phi,$$

$$\text{and } (3 \cos^2 \theta - 1) = \left(\frac{9}{4} \sin^2 \phi - 1\right).$$

$$P_{\frac{+}{-} \frac{a}{2} (1, \bar{1}, 0)}(\omega) = \int_0^\phi \frac{\sqrt{3K_1}}{2} \sin\phi \cos(\phi+\alpha) \delta\left(\omega - \Omega_R - \lambda\left(\frac{9}{4} \sin^2 \phi - 1\right)\right) d\phi \\ \frac{+}{-} \frac{a}{2} (0, \bar{1}, 1)$$

Putting $\left(\frac{9}{4} \sin^2 \phi - 1\right) = y$, we have

$$\sin \phi = \frac{2}{3} \sqrt{1+y}, \quad \cos \phi = \frac{1}{3} \sqrt{5-4y}, \quad \cos \phi \, d\phi = \frac{dy}{3\sqrt{1+y}},$$

$$\text{and } d\phi = \frac{dy}{\sqrt{(1+y)(5-4y)}}.$$

Substituting in the above equation for $P(\omega)$, we get

$$\begin{aligned} P(\omega) &= \sqrt{\frac{K_1}{3}} \int_0^{\phi_0} \frac{\cos \alpha}{3} \delta(\omega - \Omega - \lambda y) \, dy \\ &= \int_0^{\phi_0} \frac{2}{3} \sin \alpha \sqrt{\frac{1+y}{5-4y}} \delta(\omega - \Omega - \lambda y) \, dy \end{aligned}$$

The first of these two integrals is zero everywhere except at

$$y = \frac{\omega - \Omega}{\lambda} = \left(\frac{9}{4} \sin^2 \phi - 1\right)$$

Thus it makes a constant contribution to the lineshape between

$$(\omega - \Omega) = -\lambda \quad \text{and} \quad (\omega - \Omega) = 1.25\lambda.$$

The second integral has the value

$$= \frac{2}{3} \sin \alpha \left[\frac{1 + \left(\frac{\omega - \Omega}{\lambda}\right)}{5 - 4\left(\frac{\omega - \Omega}{\lambda}\right)} \right]^{1/2}.$$

This contributes to the lineshape only when $(\omega - \Omega) > -\lambda$ and reaches ∞ when $\left(\frac{\omega - \Omega}{\lambda}\right) = \frac{5}{4}$. It should be noted that $-\lambda$ and $\frac{5}{4}\lambda$ are also the extremum values that $(\omega - \Omega)$ can take on, since

$$\frac{\omega - \Omega}{\lambda} = y = \left(\frac{9}{4} \sin^2 \phi - 1\right).$$

The line shapes for the remaining six nearest neighbor sites can likewise be calculated. The end result is the adjacent

plot for the nearest neighbor lines. Thus more than 11/12 of the total intensity of nearest neighbor satellite lines lies between $\omega - \Omega_0 = 1.25\lambda$ and $-\lambda$. It should be pointed out that in the absence of anisotropic interactions contained in λ , the Zeeman frequency corresponding to the nearest neighbor satellite line is Ω_0 . Thus $\frac{\omega - \Omega_0}{\lambda}$ is a measure of the deviation of resonance frequency from its Zeeman value in units of λ .

The difference between the internal fields corresponding to the two peaks is $2.25 \lambda/\gamma$. Now we are in a position to consider the effect of the loss of moment on host atoms in the vicinity of an impurity atom, on the difference between the internal fields corresponding to the two peaks of the nearest neighbor line. Kubo and Itoh¹⁹ have recently given an expression for ΔB_{int} , the difference between internal fields at the two peaks, with the correction for the loss of moment on host atoms in the vicinity of the impurity. According to their formula

$$\Delta B_{int} = \frac{1}{r^3} \{ 2.25 (\mu_p + \mu_{imp} - \mu_0) - 3.5\Delta\mu_{1n} - 2.5\Delta\mu_{2n} - 3.5\Delta\mu_{3n} \} \quad (5)$$

where r is the nearest neighbor distance; μ_0 the cobalt moment

in pure matrix; $\Delta\mu_{in}$ ($i = 1, 2, 3$), the quantity $(\mu_{in} - \mu_0)$ for the cobalt atoms in the i th neighbor position with respect to the impurity; and the quadrupolar effects are assumed to be negligible. (Kubo and Itoh¹⁹ give a positive sign for the terms involving $\Delta\mu_{2n}$, but our calculation shows that it must be negative like the rest of the terms involving the loss of moment.) As far as the line splitting is concerned, the assumption regarding quadrupolar effects is perfectly sound and we shall adopt it for our own treatment. The dipolar field correction term is derived by evaluating fields at host nuclei of interest due to their nearest neighbor host atoms. Since ΔB corresponds to the maximum difference in B_{int} corresponding to the two sets of nearest neighbor sites, we require that for the δ -function peak the dipolar field cause maximum displacement of the line away from the other satellite component (this is "allowed" since the line shape is independent of ϕ). For the 1.251 peak, we have to use $\sin \phi = 1$ which gives us the shift for this line in the domain wall. Equation 5 is the net result. This will be used by us to evaluate the pseudo-dipolar moment for various impurities used by us in cobalt.

Finally, a word about the effect of finite linewidth on the NMR spectra. Let us assume that Δ is the linewidth of the satellite line. Clearly if $\Delta \ll \lambda$, then no splitting will be observed and a single line with contributions from all the nearest neighbor sites will be observed. On the other hand if $\Delta \gg \lambda$, all the lines will be resolved. In the intermediate range, the relationship between the satellite line height and

and the line width Δ for the various near-neighbor peaks is shown in the following plot.

Variation of the height of n. n. satellite line peak in face-centered cubic cobalt as a function of Δ .

- A: δ function peak at $\{\omega - \omega_0\} = -\lambda$
- B: line at $\omega - \omega_0 = 5\lambda/4$
- C: broad line at $\omega - \omega_0 = -\lambda$
- D: line at $\omega - \omega_0 = 2\lambda$

2.3 Nuclear Spin-Spin Relaxation in Ferromagnets

Spin-spin interactions among the nuclei result in a dephasing of the transverse precessing component of spin. This leads to a decrease in the echo amplitude with a characteristic time T_2 called the spin-spin relaxation time. In the case of

Co^{59} in natural cobalt, the dominant mechanism for spin-spin relaxation has been suggested to be the Suhl-Nakamura (S-N) interaction.^{17, 20-21} [Nuclear spin-flip due to the emission (absorption) of a virtual magnon by one nucleus and subsequent absorption (emission) by a second nucleus.] Being an indirect interaction, it is expected to give non-exponential relaxation. Weger et al.¹⁷, who found that this is not the case with Co^{59} in cobalt, have suggested that microscopic inhomogeneities tend to decouple the nuclei partially and thus lead to exponential relaxation.

The relaxation rate from the S-N interaction is given by²⁰

$$\frac{1}{T_2}_{\text{SN}} = (\Delta\nu^2)^{1/2} = S \frac{I(I+1)}{24\pi} \left(\frac{H_{\text{ex}}}{H_{\text{int}}} \right)^{1/4} \left(\frac{A}{h} \right) \left(\frac{A}{g\mu_B H_{\text{ex}}} \right)$$

where A is the hyperfine coupling constant, S the electronic spin, and all other quantities have their usual meaning. Using this formula, Stearns²² has obtained the relaxation rate in cobalt to be

$$\frac{1}{T_{\text{SN}}} = 7000 \text{ sec}^{-1}$$

At 4.2K, Weger et al.¹⁷ have measured $1/T_2$ to be $11,360 \text{ sec}^{-1}$. Thus more than half the relaxation in Co at 4.2K comes from S-N interaction. The result of this calculation should be accepted with some reservation for the following reasons:

a) The above expression was derived using the Van Vleck moment formula.²³ This is valid for interactions between spins which are well separated in frequency so that only one is excited by the rf pulse. This is certainly not the case in spin echo

experiments where rf pulses have Fourier components over a range of frequencies.

b) Domain wall effects have been completely neglected.

c) Suhl-Nakamura theory has been worked out in detail only in the case of a Heisenberg ferromagnet and the behavior of cobalt has to be regarded as being intermediate between that of a Heisenberg ferromagnet and an itinerant-electron ferromagnet.

Despite all these complications, it is probably safe to say that at 4.2K there is a significant contribution of the S-N interaction to the nuclear relaxation in cobalt. Experimental confirmation of this has been obtained by recent experiments of Shaw²⁴ and Barak and Kaplan,²⁵ who used an external magnetic field to reduce microscopic inhomogeneities and found that S-N interaction is the dominant mechanism for spin-spin relaxation in cobalt.

The effect of impurities on the spin-spin relaxation of the host Fe⁵⁷ nuclei in dilute alloys of natural Fe has been studied by Stearns.²² She has advanced a qualitative explanation for the observed shorter relaxation times at host nuclei in alloys compared with their value in pure metals: The impurities tend to act like pinning points in the domain walls. In general this decreases the enhancement factor as observed for dilute alloys²⁶ and also leads to considerable variation in the total energy of the sample depending on the domain wall position. Thus the wall may not return to the same position after each rf pulse.

This can lead to each domain wall nucleus being in a slightly different magnetic field after each pulse which would give an apparent added contribution to T_2 relaxation mechanism.

To sum up, there is no comprehensive theory that could be checked against experiments on spin-spin relaxation in cobalt alloys. The best one can hope to do is to draw conclusions about the mechanisms involved from the trends in relaxation time at different sites in each alloy system and comparison of the three alloy systems with each other in this respect.

2.4 Modulation of the Spin Echo Envelope

In pure face-centered cubic cobalt nuclear relaxation is dominated by spin-spin interaction and the spin echo envelope (the plot of echo height as a function of time between the two exciting rf pulses) is pure exponential. Under certain conditions the spin echo envelope can be modulated with a period which is dependent on the strength of interaction responsible for such modulation. In this section we examine the various interactions in alloys and their effect on the spin echo envelope of the host nuclear spins. The observed echo modulation at 172.5 MHz in Co-Cr alloy will be interpreted in the light of discussion in the present section at a later stage in this thesis.

The effect of alloying on the spin echo envelope of face-centered cubic metals lead and platinum has been studied in detail by Alloul and Froidevaux.²⁷ Although the case of ferromagnets is different from that of ordinary metals in many ways,

the basic interactions are the same. We will give an outline of their work leading to the various kinds of echo modulation observable in alloys and the relationship between the modulation period and interaction energy in different cases.

Let H be the total Hamiltonian of the nuclear spin system. The principal term in this Hamiltonian is the Zeeman term $H_z^0 = -\omega_0 \sum_j I_j^z$ where the z -axis is assumed to lie along the direction of B_{int} in the case of a ferromagnet. Static inhomogeneities which result from alloying cause the internal field to vary from site to site and introduce an additional term $H_z^1 = -\sum_j \delta\omega_j I_j^z$. In the total Hamiltonian H only terms commuting with the principal part are to be taken into account. Thus we include terms representing the quadrupolar interactions, the various spin-spin interactions, and the Hamiltonian due to the impurity spins. The total Hamiltonian can then be written as,

$$\begin{aligned} H &= H_z^0 + H_z^1 + H_q + H_{dd} + H_{ex} + H_{IS} + H_S \\ &= H_z^0 + H_z^1 + \sum_j a_j (I_j^z)^2 + \frac{1}{2} \sum_{j,k} B_{jk} (I_j \cdot I_k - 3I_j^z I_k^z) \\ &\quad + \frac{1}{2} \sum_{j,k} J_{jk} I_j \cdot I_k + \sum_{j,k} C_{jk} I_j^z S_k^z + H_S \end{aligned} \quad (I)$$

H_q represents the quadrupolar couplings, and a_j is defined by

$$a_j = [3eQ/8I(2I-1)\hbar]eq_j(3\cos^2\epsilon_j-1)$$

where eQ is quadrupolar moment of the host nucleus I and eq_j is the electric field gradient which is assumed to have axial symmetry around an axis z_j which makes an angle ϵ_j with B_{int} . H_{dd} contains both the dipolar and pseudo-dipolar interactions

between spins I and

$$B_{jk} = \frac{1}{2} \left(\gamma_I^2 h / r_{jk}^3 + b_{jk} \right) (3 \cos^2 \theta_{jk} - 1),$$

θ_{jk} being the angle between r_{jk} and the z-axis, and b_{jk} the radial part of pseudo-dipolar interaction. H_{ex} is the indirect exchange coupling between the spins I. H_{IS} represents all interactions between the resonant spins I and the non-resonant nuclear spins S. H_S includes Zeeman, quadrupolar and spin-spin terms for the S spins.

The calculation of echo envelope is carried out following the density matrix formalism of Abragam.²⁸ In this method the echo intensity at time 2τ is given by

$$E(2\tau) \propto \langle I_x \rangle_{av} \propto \text{Tr} \{ \rho(2\tau) I_x \}$$

with $\langle I_y \rangle_{av} = 0$ where $\rho(2\tau)$ is the density matrix of the whole spin system describing the motion of the spins in rotating frame, $I_x = \sum_l I_l^x$, and the trace is taken in the space of spins I and S. For the general Hamiltonian represented by equation I, calculation of $E(2\tau)$ is impossible. However, if H_{IS} can be neglected (as we believe to be the case in Co-Cr alloy because of the low natural abundance and small nuclear spin of Cr⁵³, the only non-zero spin isotope of Cr) and the inhomogeneous broadening is large compared with the spin-spin interaction,

$$\text{i.e., } |\delta\omega_j - \delta\omega_k| \gg b_{jk}, J_{jk}, \gamma_I^2 h / r_{jk}^3,$$

a condition which we believe to be satisfied for all our alloy systems; then the xy components of $I_j \cdot I_k$ average out to zero

and these terms in the spin-spin Hamiltonian are neglected. Further, the expression for $E(2\tau)$ can be calculated exactly. Under these conditions it is found that the echo envelope can be represented as a product of two factors, one involving the quadrupolar effects and the other the spin-spin interaction. Each of these factors may have oscillatory behavior. In the event that the echo envelope is modulated by both effects, a distinction between the two modulations is possible only if their modulation frequencies as well as modulation depths are sufficiently different. For spin-spin interactions alone it is found that the frequency of modulation is related to the relative value of spin-spin coupling constants J (the indirect exchange) and B (the dipolar and pseudo-dipolar coupling constant). For Co alloys, $J \gg B$,²⁹ and the modulation period is expected to be of the order of $2\pi/J$.²⁷

Modulation of the spin echo envelope in the case of a small quadrupolar interaction which can be treated as a perturbation on the large Zeeman energy has been studied by Abe *et al.*³⁰ for ferromagnetic materials. They find that the spin echo envelope of the first echo (under certain conditions multiple echoes can be observed) is modulated with the fundamental modulation period of π/a , where $a = \{3eQ/4I(2I-1)\} V_{zz}$. This has been derived under the assumption that $|\omega - \omega_0| \ll a$ and ω_1 where $\omega_1 = \gamma H_1$, H_1 being the rf field during the pulse, ω the exciting rf frequency and ω_0 the center frequency of the nuclear resonance. If this condition is not satisfied, the echo amplitude cannot be derived in an analytical form.

Stearns³¹ has recently studied the effect on echo envelope of a transverse spin-spin interaction of the Suhl-Nakamura type, i.e., $B (I_j^+ I_k^- + I_j^- I_k^+)$. Considering only two spins I_1 and I_2 , she finds that in response to a $\phi - \theta$ pulse sequence, the echo intensity is given by

$$E(2\tau) \propto \sin\phi \sin^2 \frac{\theta}{2} \left[1 + \cos\theta (1 - \cos\Delta\tau) \left(\frac{B}{\Delta}\right)^2 \right]$$

where $\Delta = \sqrt{B^2 + \delta^2}$ and $\delta = (\delta_1 - \delta_2)$, δ_1 and δ_2 being the chemical shifts for nuclei 1 and 2 respectively. (In a ferromagnet the dominant contributions to the chemical shift are of magnetic origin, i.e., result from impurities, vacancies, and dislocations). Thus modulation from such an interaction has a period of $2\pi/\Delta$. It will be large when $B \gg \delta$, attaining a maximum value for $\delta=0$. There will be no modulation if $\theta=\pi/2$ or if $\delta \gg B$. Further, it is also possible that when averaged over the entire domain wall such an effect will be completely smeared out.

To sum up we have described three mechanisms which could cause spin echo envelope modulation. Two of these have their origin in the spin-spin interaction and the third one is due to quadrupolar effects. The relevance of these to the observed echo envelope modulation will be discussed in a later chapter.

Chapter III

Experimental Set-Up and Procedures

3.1 Sample Preparation

All alloys used in this work were prepared by melting the constituent metals in the proper proportion in an induction furnace in an atmosphere of high purity argon. The crucibles used were either alumina or magnesia. (In the early stages of this work some alumina crucibles were found to react with cobalt yielding a brilliant blue coloration (probably $\text{Co}_2\text{Al}_2\text{O}_4$, Thenard's blue). This could easily be washed off with acid indicating that the effect was probably connected with surface oxidation. Use of crucibles of recrystallised alumina (AD-99 quality, coors) and operation at somewhat lower temperatures eliminated this reaction. Maybe we had been operating too close to the stability limit of alumina ($\sim 1900^\circ \text{C}$.) In each case, the contents were left well above the melting point of cobalt for at least fifteen minutes to ensure good homogeneous mixing of the impurity in the host. For best results the load used for each melt had to be below 10 grams. A portion of the cobalt load (~ 2 gms.) was powdered and mixed thoroughly with the impurity (cobalt itself was in the form of platlets). This procedure gave better homogeneity of the alloys as indicated by better nuclear spin echo signal obtained for the nearest neighbor satellite line. The molten alloy ingots were rapidly quenched in liquid nitrogen or water by pulling the crucible out of the induction furnace and immersing it in the liquid.

This procedure is necessary to get the f.c.c. phase rather than the hexagonal one which begins to form below 600°C in Co-Cr, 500°C in Co-V, and 400°C in Co-Mn for 2% alloys, which is the approximate concentration in our samples.³² The compositions of the alloys, based on the quantities of constituents used, are: Co-Cr 1.4%; Co-V 2%; and Co-Mn 2%. This composition should not be taken too seriously as no analysis could be performed on the alloy ingots and the vapor pressures of Cr and Mn are an order of magnitude higher than that of cobalt at the same temperature.³³ Thus at least in these two alloys the composition is definitely going to be less than that originally planned. This has no effect on the results of this work and shall not be pursued any further.

The Co-Cr alloys was filed by our automatic filing machine described in the Appendix. For other alloys, the sample ingot was mounted in a lathe operated at slow speed and filing with a #2 file. The filings collected were rather coarse (less than 10% of it was finer than 325 mesh). Finer powder was obtained by grinding them in a ball mill using tungsten carbide balls. This method of filing, although much faster than the automatic filing machine gave only 25-30% powder of the desired size whereas in the former method, approximately 90% of the powder was finer than 325 mesh.

At this stage the alloys were looked at with CW tunnel diode NMR spectrometer for Co^{59} line but none was observed, apparently because of the strains introduced in filing and grinding process. Annealing treatment was given next in order

to remove these strains. This was done as follows: The alloy powder was thoroughly mixed with approximately four times its volume of alumina powder to avoid sintering of alloy particles, annealed in an atmosphere of a mixture of 95% argon - 5% hydrogen, and finally quenched in approximately 15 minutes under flowing gas.

For Co-Cr alloy it was found that annealing at 1000°C for 24 hours improved the signal to noise ratio for nuclear spin echo signal at the nearest neighbor satellite line by a factor of 3 compared with that annealed at 700°C for the same length of time. The echo signal at 77 K could easily be seen directly on the oscilloscope and no further attempt was made to improve it. (One reason why this was not done was that despite mixing the alloy with alumina powder, the alloy particles tended to sinter together during the anneal at this high temperature so that the quantity of 325 mesh powder was reduced at the end of each anneal.)

For Co-V however an anneal at 1000°C for one day resulted in complete disappearance of the satellite line. Samples were annealed at 800°C for three hours and at 700°C for 1 1/2 hours and it was found that sample annealed at 700°C showed a better satellite line echo signal than the one annealed at 800°C . Such anomalous behavior for these alloys has also been reported by Reidi et al.⁵ The line shapes for the sample annealed at 800°C are sharper compared with those of the sample annealed at 700°C , as expected. The frequencies corresponding to the various satellite lines are the same in the two samples. The decrease

in echo intensity on annealing at a higher temperature is hard to explain on the basis of the phase diagram of this alloy system and we will not worry about it. The results reported are for the alloy annealed at 800°C for 3 hours.

For Co-Mn alloy again annealing was required at 1000°C for 24 hours to get a reasonably good satellite line spin echo signal at 4.2 K. The signal at 77 K could not be observed without a box-car integrator.

3.2 CW vs Pulsed Methods of NMR Detection

In this work, we have used a CW tunnel diode NMR spectrometer and a coherent spin echo spectrometer. These are described in the next two sections of this chapter. Here we give the relative merits and demerits of the two methods for the study of line shapes in ferromagnetic alloys. The main problem encountered in nuclear resonance work in ferromagnets is the discrimination of true NMR signals from background spurious resonances. This discrimination in the case of CW and spin echo techniques has been treated by Scurlock et al.³⁴

Let $\alpha = \frac{\text{width of background resonance}}{\text{width of nuclear resonance}}$; then in the case of our tunnel diode CW spectrometer, the nuclear resonance can be observed unambiguously only if $\alpha > 1$, i.e., the nuclear resonance is sharp compared with a spurious resonance. For spin echo a discrimination is possible even when $\alpha < 1$. Let us define

$$T_n = \frac{1}{2\pi(\Delta f)_n}, \text{ where } (\Delta f)_n = \text{width of nuclear signal at half height}$$

$$T_B = \frac{1}{2\pi(\Delta f)_B}, \text{ where } (\Delta f)_B = \text{width of background signal at half height}$$

For ferromagnets and their alloys, there is considerable inhomogeneous broadening of the NMR lines. Thus $T_2 \gg T_n$. If $T_B \sim T_n$, we can write

η = discrimination ratio of signal/background

$$\begin{aligned} &= \frac{e^{-t/T_2}}{e^{-t/T_B}} \\ &= \exp t/T_2 \left(\frac{T_2}{T_B} - 1 \right) \\ &= \exp t/T_2 \left(\alpha \frac{T_2}{T_n} - 1 \right) \end{aligned}$$

For the alloy systems studied by us, $T_2 \sim 100$ μ sec and $T_n < 1$ μ sec for all the satellite lines. Thus,

$$\eta \gtrsim \exp t/T_2 (100\alpha)$$

For $t = T_2$, $\eta \gtrsim \exp (100\alpha)$

Thus for broad lines, as is the case in this work, there is considerable advantage to using the spin echo method compared with a cw method.

The cw method is superior to spin echo method for sharp lines if spurious resonances can be eliminated from the spectrometer output. Furthermore, it is simple to set up for a scan over a wide range of frequencies and the lineshape is recorded directly on the strip chart recorder. On the other hand our spin echo spectrometer requires the use of a point by point scan method which involves relatively laborious procedure for extracting line shape. The two methods were used to complement each other in our experiments. After each anneal, Co⁵⁹ main

resonance which occurs at 213.1 MHz at room temperature, in face-centered cubic cobalt, was looked at with the cw set-up. Its line shape and structure around it could be used to ascertain the homogeneity as well as the state of anneal of the alloy. (For Co-Cr and Co-V alloys two satellite lines were observed in room temperature spectra on the low frequency side of the cobalt main line between 200-210 MHz. Since the lines are weak, their assignment to any impurity neighbor configuration is not possible. For those samples in which these satellite lines were not observed, no satellite was observed with the spin echo set-up at low temperature. Thus it was a good and quick test for these samples.) Unfortunately our tunnel diode NMR spectrometer could only be used to to 77 K whereas the spin echo set-up could be used with the sample at 4.2 K. All studies of NMR spectra reported in this work were done at 4.2 K using spin echo spectrometer.

3.3 Tunnel Diode NMR Spectrometer

A block diagram of our tunnel diode NMR spectrometer is shown in Fig. 1. The set up beyond the tunnel diode oscillator and its associated biasing voltages is conventional and will not be dealt with in any detail. The use of a tunnel diode oscillator as an NMR detector has not been reported in the literature and we shall describe it in some detail. The oscillator is of the swept-frequency, frequency-modulated type. It consists of an inductance coil and a varactor diode forming the tank circuit with a tunnel diode, TD-9 (G.E. Germanium, 1/2 ma), providing the negative resistance. By proper choice of inductance and the

BLOCK DIAGRAM OF TUNNEL DIODE NMR SPECTROMETER

Fig. 1.

TUNNEL DIODE OSCILLATOR CIRCUIT

Fig. 2. C's are 500 pf Eria silver-mica capacitors, F's are Eria filtercoons #1202 and B the ferrite beads.

varactor diode, mounted in a suitable configuration (to eliminate spurious resonances), a wide range of frequencies has been covered. For the purposes of this work operation in the 200 MHz range was desired. The varactor used was VA-211 (Crystallonics, high Q, $V_{\text{breakdown}} \approx 160\text{V}$, 10 pF at -4V) along with a 5 turn Cu strip coil, 1/4" diameter, 1 1/4" long. A circuit diagram showing layout of the tunnel diode oscillator is given in Fig. 2. The entire oscillator is housed in an aluminum box milled out of solid aluminum block with dimensions 6" x 2" x 1 1/4". It has five chambers completely shielded from each other as shown by dotted lines in the figure. Frequency modulation is produced by applying to the varactor a dc bias voltage modulated with a suitable ac obtained from the PAR lock-in amplifier. The modulation voltage is decreased with the dc bias voltage through the use of a ganged set of potentiometers as shown in the Appendix. Thus the dc bias and ac modulation are always in the same proportion. (The capacitance of a varactor as a function of applied reverse voltage is approximately given by³⁵

$$C_v \approx \frac{C_o}{(V + 1/2)^{1/2}}$$

where C_o = capacitance at zero voltage. At small values of V, it increases very rapidly. Thus at low values of V, the same value of ΔV will cause a much greater ΔC and consequently Δf than at large values of V.) The biasing voltage for the tunnel diode is obtained from a 0-1 volt, constant voltage power supply. A circuit diagram of the same is given in the Appendix. For the work reported in this thesis, a bias voltage of 100

milli-volts was used. The swept-frequency operation of the oscillator is achieved by varying the varactor bias voltage using a standard motor-gearbox arrangement.

The basic equation governing the operation of a tunnel diode oscillator is the oscillation condition,

$$\frac{C R_T}{1 - g_d} < L_T$$

where $C = (C_v + C_d)$, C_v and C_d being the capacitance of the varactor and the tunnel diode respectively, R_T and L_T the total resistance and the total inductance in the circuit respectively, and g_d the transconductance of the tunnel diode at the operating point. When this condition is satisfied, the oscillation frequency is given by

$$f = \frac{1}{2\pi\sqrt{L(C_v + C_d)}}$$

The level of oscillation can be controlled to some extent by changing the bias voltage across the tunnel diode, which varies g_d . Marginal operation for maximum sensitivity can be achieved by staying close to the oscillation condition, i.e., using the smallest permissible value of L .

Spurious resonances can be prevented by the use of ferrite beads at certain points in the circuit. Thus for operation around 200 MHz required for this work, a ferrite bead introduced on the tunnel diode lead on the inductance side gives a very "clean" base line from ~220 MHz to ~160 MHz.

The oscillator has two distinct advantages over the conventional cw spectrometers:³⁶

- a) The oscillator itself is housed in a small volume. The problems associated with line resonances are thus eliminated.
- b) The level of oscillations is inherently low and can be easily controlled by proper choice of L and the varactor diode. Thus saturation of nuclear resonance is never a problem.

The spectrometer has been used by us successfully down to 77 K. At 4.2 K the varactors used show no capacitance variation as a function of voltage. This might be due to the fact that the conduction electrons are completely frozen out at this low temperature. Even if we had been able to operate it at 4.2 K, it probably could not have given us any more information on satellite lines than we have been able to derive from the spin echo study.

The spectrometer was extremely useful for quick checks of alloys used in this work as mentioned earlier.

3.4 Spin Echo Spectrometer

A block diagram of our coherent spin echo spectrometer is shown in Fig. 3. A similar set-up using an incoherent pulsed oscillator has been described in detail by Houghton.³⁷

A coherent pair of pulses is produced by gating the pulsed output of a very high frequency (VHF) signal generator (Hewlett Packard Model 608D) using a diode switch (Philco Model P.S. 9018) with a pair of pulses suitably biased from a modular pulse generator (General Radio Model 1395 A). The modular pulse generator has five pulse/delay units. The first of these is used to generate a 0 - +5 volt pulse required to trigger the VHF signal generator in the pulse mode. The second unit is

Fig. 3. Block diagram of Spin Echo Spectrometer,
 $(t_1+t_2+2\tau) > T > (t_1+t_2+\tau)$.

used to generate a delay of approximately 0.5 μ second between the initiation of the trigger pulse of unit I and the start of pulse in unit III. This is done to ensure that the rf output of the VHF signal generator has attained its peak value before the application of the pair of pulses generated in the last three units of the modular pulse generator. The dc level of the two pulse sequence has to be adjusted so that the RF leakage at the output of the diode switch is minimum in the absence of pulses, while sufficient peak power is obtained when pulses are applied. The rf at the output of the diode switch is fed into an rf power amplifier (Hewlett Packard Model 230A). A 3 db attenuator is used at the output of the rf power amplifier to protect it against damage due to reflections resulting from any mismatch in the sample tank circuit. The pulses are fed through a directional coupler which enables measurement of incident rf power through the use of a crystal detector (Hewlett Packard Model 423A) and matched resistor load (Hewlett Packard Model 11523A). The output of the directional coupler goes into a hybrid junction (Anzac Model H-9), one arm of which has a standard 50 Ω termination and the other is connected to a coaxial line leading to the tank circuit (containing the sample) through a capacitive coupling. The tank circuit along with the coupling capacitor (Fig. 4) are mounted below a brass plate 2" in diameter. It is rigidly connected to an 8" diameter brass flange at the top of our helium dewar through a 24" long, 1/2" diameter thin wall stainless steel tube. The tuning capacitor (E.F. Johnson, #160-104, 1.8-8.7 pf) is screwed onto the 2"

Fig. 4. Schematic diagram of the tank circuit set-up (not drawn to scale).

brass plate and is varied by means of a 1/8" stainless steel tube soldered onto it and going through a quick connect in the top plate. The coupling capacitor is a homemade cylindrical capacitor with a teflon dielectric. The inner cylinder of this capacitor is connected to the center conductor of the 50 Ω coaxial line (again home-made) feeding the rf pulses to the tank circuit. The outer conductor of this coaxial line is a 3/8" stainless tubing which goes through a quick-connect in the top plate and a finger-stock contact ring which is soldered to the 2" brass plate. The outer cylinder of the coupling capacitor is kept fixed by means of a semi-rigid connection to the tuning capacitor. The coupling capacity is varied by sliding the coax in and out, thus varying the effective area. Aluminum foil is wrapped around the tank circuit to ensure its isolation from the surroundings.

The output of the hybrid junction is connected thru a couple of variable attenuators (Hewlett Packard Models 355C and 355D) which enable an attenuation of more than 100 db to be introduced in steps of 1 db into a power limiter (Microwave Associates Model MA 8445-T11) and then a balanced mixer (Anzac HFK 20RW). The other input of the mixer is fed from the local oscillator (General Radio Model 1215B) a frequency ± 30 MHz off from that of the VHF signal generator. The output of the balanced mixer goes into a 30 MHz IF amplifier, with a built-in video detector, (Varian Model IMM2) whose output is then fed into a boxcar integrator (PAR Model CW-1) or the scope.

The shortest pulses obtainable at maximum power were 0.5

μ sec long and the maximum power was found to be ~ 4.5 watts. Only a fraction of this power was needed for most of our work.

The procedure for setting up the spectrometer was as follows: The tank circuit containing the sample was first adjusted to be at the correct frequency and to present a correct impedance (50Ω) at that frequency. This was done by using a sweep generator in conjunction with an impedance bridge (Telsonic Model TRB-3) and an oscilloscope by comparison with a standard 50Ω termination. Next with the VHF signal generator tuned to the correct frequency ν , the power amplifier was tuned to it. This was done by maximising the rf pulse amplitude at the input of the directional coupler. The next step was to adjust the local oscillator frequency to be $(\nu \pm 30)$ MHz. This was done by replacing the tank circuit connected to the hybrid junction by a 50Ω termination. The rf pulses were generated and the output of the IF amplifier maximised by adjusting the local oscillator frequency. (Since the large gain of the IF amplifier causes saturation of the IF output, an attenuation of ~ 50 db has to be introduced to prevent saturation and to enable the output to be correctly maximised.) The tank circuit was then introduced and adjusted so that the IF output was minimum. This implies that resonance absorption of incident rf power is taking place in the tank circuit.

The spectrometer is now ready for operation. Removal of attenuation should give an echo if the frequency is right. Minor adjustments may be necessary for maximising the echo amplitude.

3.5 NMR Spectra using Spin Echo Spectrometer

Before going into the details of actually obtaining NMR spectra with the spin echo spectrometer, it seems worthwhile to say a few words about the development of nuclear spin echo technique as a method for obtaining NMR spectra of ferromagnetic alloys.

The spin echo technique was originally developed by Hahn³⁸ to study the dynamical character of nuclear resonance through a measurement of spin-lattice and spin-spin relaxation times T_1 and T_2 respectively. Asayama³⁹ and Abe *et al.*⁴⁰ almost simultaneously were the first to use the nuclear spin echo technique for the study of inhomogeneously broadened NMR lines in ferromagnetic alloys. Streever and Uriano¹⁰ in a subsequent paper gave a detailed account of the use of nuclear spin echo method for the study of line shapes of inhomogeneously broadened NMR lines in ferromagnetic alloys. The technique involves measurement of echo height as a function of frequency across the inhomogeneously broadened line. Two pulses of equal width are used since in a ferromagnetic metal, as a result of skin depth and the distribution of enhancement factors in the wall, the 90° - 180° pulse condition is never satisfied for all the nuclei. The width of the pulses is determined by the resolution required. (For best reproduction of line shapes the criterion is that the distribution of frequencies in the pulse should be less than the line width so that only a portion of the inhomogeneously broadened line is excited at each point across the line.) The pulse separation is kept small so that T_2 decay effects can be

ignored. At each point the rf level of the oscillator is adjusted so as to maximise the echo amplitude. To the set of echo frequency versus echo amplitude data thus obtained, one has to apply corrections for:

- i) Greater polarisation of nuclei at higher ω .
- ii) Greater signal induced in the coil at higher ω .

Thus the correction factor will be $1/\omega^2$.

A further correction that may seem necessary at first is due to the variation of enhancement factor as a function of ω . However, the need for such a correction is eliminated if the rf level at each frequency has been adjusted to an echo maximum. For a broad distribution of hyperfine fields, effects of variation in T_1 with frequency should also be corrected for.

It should be emphasized that low rf power and sufficiently long pulses are the key to the reproducibility of line shapes. Although Streever and Uriano¹⁰ did not emphasize it, later work of Mims⁴¹ and Budnick and Skalski⁴² has shown convincingly that this is so. If the pulses are short and rf power high, this leads to complex large turn angle effects on the echo shape and reduces the reliability of data for line shapes.

With these considerations in mind, our data for NMR spectra were taken using two rf pulses, each approximately 1 μ s wide, and separated by approximately 5 μ s (the shortest T_2 being ~ 30 μ sec). A pulse width of 1 μ s was used as a compromise between good resolution and a good signal-to-noise ratio at all frequencies of interest. This is certainly in accordance with the resolution criterion mentioned above for all the satellite

lines but the line shape for the cobalt main line should not be taken too seriously for all the alloy systems. (For Co-Cr, the Co^{59} main line was considerably (~ 5 times) broadened compared with that in pure cobalt as seen by the tunnel diode spectrometer. On the other hand the main line in Co-V and Co-Mn alloys did not show any significant broadening. In the spin-echo spectra the main line appears to have the same width for all three alloys because the resolution is limited by the spectrum of the exciting rf pulses. T_1 does not vary significantly over the entire frequency range of interest and its effects have been ignored. Observations were taken at 1 MHz intervals for Co-Cr and Co-V alloys and at 1/2 MHz intervals for Co-Mn alloy over the entire frequency range of interest. (The 1/2 MHz interval was used for Co-Mn as the frequency range of interest is $\sim 1/4$ th that of the other two systems and the echo amplitude variations are much more rapid.) At each excitation frequency, the echo amplitude was maximized by tuning the local oscillator, the tank circuit, and by adjusting the rf level of the VHF signal generator. The echo height was measured directly on the scope and was properly attenuated at the output of the hybrid junction so as to lie in the linear response region of the IF amplifier. To the echo height versus frequency data thus obtained, the $1/\omega^2$ correction was applied to get the true NMR spectra.

3.6 Measurements of Nuclear Spin-Spin Relaxation Time T_2

This was done by the standard method of observing the echo

height as a function of τ , the time between the two pulses. Multiple exposure pictures of the echo were taken as τ was varied, the sweep on the scope being triggered by the second pulse. The echo height for different values of τ was read from the photographs. Modulation of the spin echo envelope, if any, could be observed directly on the photograph.

There was a little problem in using our coherent spin echo spectrometer for such continuous variation of τ . As mentioned earlier, the coherent pair of pulses are produced by gating the pulsed output of the VHF signal generator. Since we do not want any rf leakage from the diode switch when the echo is being observed, the VHF signal generator must be turned off before the echo appears. This restricts the extent to which τ can be varied without changing the width of the trigger pulse of the VHG signal generator. This difficulty was avoided by constructing a multivibrator circuit which turns the VHF signal generator on before the first pulse and off at the end of the second pulse. A circuit diagram of the same is given in the Appendix. The output of the multivibrator circuit is a -5 to +5 volt rectangular pulse which is adequate to keep the VHF signal generator on for the duration of the pulse. The pulse is initiated by a 0.1 μ s, 2 volt pulse from the first unit of the modular pulse generator and terminated with the delay output of the last unit in the modular pulse generator.

Data were taken on echo decay at the peaks of all satellite lines and the main line in each alloy system. Pulses of approximately equal width were used. Again sufficient attenuation of

the echo signal was introduced to ensure linear response of the IF amplifier to the echo signal observed on the scope.

A modulation was clearly observable in the multiple exposure pictures of the echo envelope at 172.5 MHz in Co-Cr alloy. The depth of modulation was found to increase as the exciting pulses were made narrower and the rf level higher. The shortest pulses obtainable in our coherent spin echo spectrometer were 0.5 μ s wide at 4.5 W. An incoherent pulsed oscillator was used to generate rf pulses 0.3 μ s wide with power of up to 100 W, to see if any improvement in the echo envelope modulation was observed. None was observed. It was thus felt that output pulses from the coherent set-up should be adequate in looking for the echo envelope modulation effect if any existed. This was done for satellite lines as well as the main cobalt line in all the three alloys. The results are discussed in the next chapter.

Chapter IV

Results and Discussion

4.1 NMR Spectra

These were taken using the spin echo spectrometer as outlined in section 3.5. We discuss the results for the three alloy systems under separate subheadings.

a) Co-Cr: The NMR spectrum for this alloy system is shown in Fig. 5. It is characterized by three satellite lines at 172.5 ± 0.3 , 181.0 ± 0.3 , and 213.5 ± 1.0 MHz in addition to the main cobalt line at (217.4 ± 0.3) MHz. The errors represent the change in local oscillator frequency required for a discernable change in the maximized echo height and is due to the finite bandwidth of the local oscillator. For the satellite line at 213.5 MHz, the error assigned is much larger than in the other two cases because of the relative broadness of this line and its proximity to the cobalt main line. Let us denote the satellite lines as ν_1 (213.5 MHz), ν_2 (181.0 MHz), and ν_3 (172.5 MHz). We estimate the areas under ν_1 , ν_2 , and ν_3 from the NMR spectrum and find that

$$\frac{A_1}{A_2 + A_3} = 2.3$$

where A_i is the area under the peak at ν_i ($i=1,2,3$). This is in reasonable agreement with the expected value of 2 for face-centered cubic cobalt (there are 12 nearest neighbors and 24 third nearest neighbors) if the satellite line ν_1 is assumed to come from cobalt atoms in the third nearest neighbor shell

Fig. 5

around the impurity, and ν_2 and ν_3 are due to cobalt atoms in the nearest neighbor position with respect to the impurity. Since ν_3 is the farthest of all satellite lines from the cobalt main line (217.4 ± 0.3 MHz at 4.2 K), it has to be attributed to host atoms in the nearest neighbor position around an impurity atom. The line ν_2 could possibly come from cobalt atoms which are second nearest neighbors to an impurity, or possibly from cobalt atoms in the hexagonal closed pack structure which have an impurity atom as their nearest neighbor. Both these possibilities can be rejected using intensity considerations as follows: The CW spectrum of Co^{59} main line gives us an estimate for the ratio of face-centered cubic to hexagonal closed pack cobalt in our sample to be λ^4 . Furthermore the area under the peak for second nearest neighbors (six in all) should be half that of the nearest neighbor line. Experimentally the area under ν_2 is nearly twice the area under ν_3 . Thus we conclude that the satellite lines ν_2 and ν_3 both are due to the cobalt atoms which are nearest neighbors to an impurity.

Having shown that the satellite lines ν_2 and ν_3 come from cobalt atoms in the nearest neighbor shell around the impurity, we suggest that these lines are the doublet resulting from dipolar and pseudo-dipolar interactions of the impurity acting on the host atoms in its nearest-neighbor position as predicted by the Murray-Marshall theory of NMR in dilute ferromagnetic alloys (section 2.2). The reader will recall that the theory predicts that the two components are $(\Omega_0 - \lambda)$ and $(\Omega_0 + 1.25\lambda)$, where λ is given by

$$\lambda = \gamma \frac{\mu_d + \mu_p}{|R|^3}$$

μ_d being the impurity dipole moment in the lattice and μ_p its pseudo-dipolar moment. Since μ_d is negative (since the impurity acts like a magnetic defect) as is the hyperfine field in cobalt, we attribute the lower frequency (172.5 MHz) to the $(\Omega_0 - \lambda)$ component and the other one (181.0 MHz) to the $(\Omega_0 + 1.25\lambda)$ component of the doublet. This gives us for the value of the Zeeman frequency Ω_0 for the nearest neighbor line 176.3 ± 0.4 MHz.

Furthermore using the relation for ΔB_{int} for the two peaks (Section 2.2), i.e., $\Delta B_{int} = 1/r^3 (2.25(\mu_p + \mu_{imp} - \mu_0) - 3.5\Delta\mu_{1n} - 2.5\Delta\mu_{2n} - 3.5\Delta\mu_{3n})$ we calculate the pseudo-dipolar moment of a Cr impurity in cobalt to be

$$\mu_p = 6.1 \pm 0.7 \mu_B$$

In this calculation the value of μ_{imp} used has been $0.45 \pm 0.70 \mu_B$ as determined by Cable and Hicks⁸ by their neutron diffraction experiments. The values of $\Delta\mu_{in}$ ($i=1,2,3$) have been calculated under the assumption that the internal field at a cobalt nucleus is proportional to the local moment on that cobalt atom. This gives us $\Delta\mu_{1n}$ and $\Delta\mu_{3n}$ immediately since the Zeeman frequencies are known. To get $\Delta\mu_{2n}$ we make use of the saturation magnetisation measurements on this alloy. As mentioned in Section 2.1, the addition of each impurity atom leads to a loss of $5.4 \mu_B$ in this alloy system. Thus we can write

$$6.4 = \sum_{\alpha=1}^3 N_{\alpha} \Delta\mu_{\alpha n} + (\mu_h - \mu_i)$$

Here N_α is the number of host atoms in the α th shell around the impurity, $\Delta\mu_{\alpha n}$ is the loss of moment on each host atom in this shell, μ_h is the host moment, and μ_i the impurity moment. It is assumed that atoms beyond third nearest neighbors do not suffer appreciable loss of moment. All other quantities are known, so $\Delta\mu_{2n}$ is calculated. The value of $\Delta\mu_2$ turns out to be $(-0.10 \pm 0.12 \mu_B)$ which seems to be reasonable considering that $\Delta\mu_1 = -0.32 \mu_B$ and $\Delta\mu_3 = -0.03 \mu_B$. The large error is due entirely to the error in the value of Cr moment in the alloy which has been reported to be $0.45 \pm 0.70 \mu_B$.⁸

Before concluding this discussion on Co-Cr, it should be mentioned that neither the third neighbor satellite line nor the splitting of nearest neighbor line had previously been reported. As a matter of fact the only work reported on this alloy was done at 77 K and a single satellite line was observed. Kobayashi et al.⁴, who performed these experiments, found the frequency of this satellite line to be 177 MHz in a 1.2% alloy and 172 MHz in a 5% alloy. The line at 177 MHz seems to be close to the Zeeman frequency found in our work (176.3 MHz) indicating that possibly the two lines were not properly resolved in their experiment. We have not studied the concentration dependence of satellite lines in our work and so are not in a position to comment on that aspect of their work. However, another aspect of Kobayashi work which we do not agree with is their finding that the cobalt main line is shifted towards the low frequency side. We find that within experimental errors the main cobalt line is unshifted in Co-Cr alloys compared with

its position in pure cobalt. It is possible that the unresolved third nearest neighbor line was responsible for an apparent shift in the resonance frequency of the main line in their experiments.

The spectrum does not show any clearly resolved satellite line due to second nearest neighbor cobalt atoms around the impurity. In principle, the line shape for the same can be deduced once reasonable lines for ν_1 , ν_2 , ν_3 and ν_0 (the cobalt main line) have been drawn. Such attempts in the present case lead us to believe that information derived thus cannot be regarded as reliable since it is sensitively dependent on the assumed line shape for ν_1 and ν_2 . Such procedure does seem to indicate the possible existence of second neighbor line(s) between 188-197 MHz.

b) Co-V: The NMR spectrum is shown in Fig. 6. As in the case of Co-Cr alloy the spectrum is characterised by three satellite lines at 212.0 ± 0.5 , 183.0 ± 0.3 , and 176.0 ± 0.3 MHz. As before we label these as ν_1 , ν_2 , and ν_3 respectively. Then we find by integrated intensity measurements that

$$\frac{A_1}{A_2 + A_3} = 2.4$$

which again supports the conjecture that ν_1 comes from cobalt nuclei in the third nearest neighbor position from the impurity and both ν_2 and ν_3 are from cobalt nuclei which are nearest neighbors to an impurity atom. Carrying out calculations along lines similar to that in Co-Cr, we find the Zeeman frequency of the nearest neighbor satellite line to be 179.0 ± 0.4 MHz and

Fig. 6

the pseudo-dipolar moment for vanadium impurity in cobalt to be $-4.3 \pm 0.7 \mu_B$. Kobayashi *et al.*⁴ have reported a satellite line at 175 MHz in a 1% Co-V alloy which was shifted to 172 MHz for 3% alloy at 77 K. Reidi *et al.*⁵ have found two satellite lines in Co-V alloys, one at 176 MHz and the other one at 212 MHz. They further found that the frequencies of these lines are independent of vanadium concentration. The frequencies of these two lines are in agreement with ν_3 and ν_1 detected by us. Not knowing the sensitivity and resolution of their apparatus, it is hard for us to conjecture as to why they did not observe ν_2 . Our experiment thus represents the first observation of a rather large pseudo-dipolar effect in Co-V (and for that matter in Co-Cr) alloy. A similar observation of a large pseudo-dipolar effect has recently been reported by Kubo and Itoh¹⁹ for the case of very dilute ($\sim 0.1\%$) Co-W and Co-Mo alloys. The discussion concerning second nearest neighbor line(s) given for Co-Cr alloys is applicable to the present case also. In this case the second neighbor satellite line(s) seem to be in the 190-200 MHz range.

Finally we would like to make a few comments about the NMR spectra for Co-V and Co-Cr. For both these alloys ν_3 is sharper than ν_2 although the difference is much more pronounced in the case of Co-Cr than for Co-V. Further, in the case of Co-V the anisotropic interaction energy λ is smaller and Δ , the line-width, larger than that for Co-Cr. The height of ν_3 is approximately equal to that of ν_2 for Co-V whereas the peak of ν_3 is higher than that of ν_2 in the case of Co-Cr. These factors are

consistent with the effect of finite linewidth on the NMR spectrum as predicted by the Murray-Marshall theory and represented in a plot at the end of Sec. 2.2. Further, since there are eight sites contributing to ν_2 and three to ν_3 , the integrated intensity ratio should be ~ 2.66 . The observed values are 1.9 for Co-Cr and 1.7 for Co-V. Considering that there is considerable overlap of ν_3 with ν_2 and of ν_2 with ν_1 the agreement has to be regarded as reasonable.

Thus we feel that the spectra observed in these two alloy systems are in fair agreement with the prediction in the Murray-Marshall theory (Sec. 2.2).

c) Co-Mn: The NMR spectrum for this alloy is shown in Fig. 7. In this case only one satellite line at 209.5 ± 0.3 MHz is observed. We assume this to be the nearest neighbor line. A noticeable bump around 215 MHz may be the location of third nearest neighbor line but its closeness to the cobalt main line makes any intensity measurements and consequently correct assignment to a certain impurity neighboring configuration quite difficult. The fact that the nearest neighbor satellite line is not split as in the case of Co-Cr and Co-V alloys indicates that the pseudo-dipolar effect is very small. This seems reasonable as the introduction of Mn in cobalt causes a loss of moment of $4.5 \mu_B$. Out of this $2.7 \mu_B$ can be explained on the basis of host-impurity moment difference. Thus there is only $1.8 \mu_B$ loss on neighboring atoms (compare $5.1 \mu_B$ for Co-Cr and $4.3 \mu_B$ for Co-V). The small loss of moment is expected to have been caused by a small distortion of d-shells and hence the

Fig. 7

small pseudo-dipolar moment. The absence of any splitting in the nearest neighbor line gives us for an upper limit on μ_p ,

$$\mu_p \lesssim 1.9 \pm 0.7 \mu_B$$

4.2 A Phenomenological Model for Hyperfine Fields in the Alloys

In cobalt, the nuclear magnetic resonance frequency ν is related to the field B at the nucleus by the relation⁴³

$$\nu(\text{MHz}) = 1.01 B (\text{kG})$$

Thus the NMR spectra obtained give us the distribution of the hyperfine fields at cobalt nuclei in the alloys. In ferromagnets large internal fields are known to arise from the 3d moment of the atoms which cause a polarisation of the core s electrons and conduction s electrons leading to internal fields through the Fermi contact interaction.⁴⁴

In this section we will make an attempt to obtain some form of correlation between the observed hyperfine fields at cobalt nuclei at various neighboring sites around the impurity in the three alloy systems studied and the distribution of magnetic moments around the impurity. We assume, following Streever and Uriano¹⁰ and Kobayashi et al.⁴ that the hyperfine field at cobalt nuclei in cobalt rich alloys can be represented as a sum of two terms, one proportional to the self moment of the atom in question and the other to the average magnetic moment of the alloy. Thus one writes

$$B_{\text{int}} = (a \mu_{\text{self}} + b \bar{\mu})$$

Using the data for Co-Ni alloys the constants a and b are estimated to be $39 \text{ Koe}/\mu_B$ and $88 \text{ Koe}/\mu_B$ respectively. The reason why a Co-Ni alloy is used for determining the constants a and b is that it lies on the Slater-Pauling curve and the magnetic moment on both cobalt and nickel remains unaltered on alloying. The above expression predicts correct values of B_{int} for the hyperfine field at both nickel and cobalt nuclei in cobalt-nickel alloys over a wide range of concentrations. For fields at cobalt nuclei in the nearest neighbor position around an impurity, $\bar{\mu}$ needs to be replaced by the average moment on the nearest neighbor shell of the host (if only atoms in the nearest neighbor shell are assumed to make a significant contribution to B_{int}). Then

$$B_{\text{int}} = (a \mu_{\text{self}} + b' \sum \mu_{\text{n.n}})$$

where the sum extends over all the nearest neighbor atoms. The constants a and b' are determined by using the value of B_{int} in pure cobalt and at Co near neighbor satellite line in Co-Ni.

We get

$$a = -37 \text{ kG}/\mu_B \text{ and } b' = -7.5 \text{ kG}/\mu_B$$

It should be pointed out that Co-Ni is an exceedingly simple magnetic system in that the magnetic moment disturbance is localized at the impurity itself. For alloys investigated in this work this is not true and B_{int} may include terms representing the contribution of farther than nearest neighbors. Nevertheless, the above phenomenological equation should be good to a first order approximation.

In order to estimate the shift in the hyperfine field at cobalt nuclei which are in different neighbor positions with respect to the impurity, we need to know the loss of moment for cobalt nuclei in the first, second and third neighbor shells around the impurity. (We assume that for fourth and farther neighbors the loss of moment is negligible.) Since no direct measurements on these are available, we adopt the following different methods to estimate the hyperfine field shifts:

- a) Use the magnetic moment disturbance parameters employed by Cable and Hicks⁸ in fitting their neutron scattering data on these alloys as representing the loss of moment at cobalt atoms in the vicinity of the impurity.
- b) Assume that the internal field at a given cobalt atom in the alloy is proportional to its moment. This amounts to saying that the relative contribution of the two terms in B_{int} is the same for all cobalt atoms and as a first approximation this does seem to be reasonable. The method for calculating $\Delta\mu_1$, $\Delta\mu_2$, and $\Delta\mu_3$ under this assumption has been outlined in the previous section.
- c) Use a combination of a) and b). Assumptions a) and b) lead to somewhat unrealistic values of $\Delta\mu_i$ ($i=1,2,3$). For a) the magnetic moment disturbance turns out to be larger at the second nearest neighbors than it is at the nearest neighbors which does not seem to be physically sound. Working with assumption b) leads us to a larger magnetic moment disturbance at the third neighbors than at second neighbors in the case of

Co-V. Thus as a compromise between the two pictures we assume that significant loss of moment occurs only out to second nearest neighbors and that the shift in internal fields at the nuclei of cobalt atoms which are nearest neighbors to an impurity is proportional to the loss of moment suffered by these atoms.

The values of ΔB thus calculated for Zeeman frequencies of the various neighboring satellite lines in the three alloys are tabulated below.

TABLE 1*

METHOD Alloy	a			b			c			EXP.		
	ΔB_1	ΔB_2	ΔB_3	ΔB_1	ΔB_2	ΔB_3	ΔB_1	ΔB_2	ΔB_3	ΔB_1	ΔB_2	ΔB_3
<u>Co-V</u>	32.3	21.0	6.7	32.4	14.2	6.7	34.1	17.8	6.5	40.7	25	3.9
<u>Co</u>	± 6.2	± 4.1	± 1.2	± 6.0	± 4.4	± 0.9	± 6.0	± 4.8	± 1.0	± 0.5	± 5	± 1.0
<u>Co</u>	34.4	19.4	6.2	33.5	8.7	5.2	34.7	13.5	5.4	37.7	22	5.5
<u>Co</u>	± 6.0	± 4.1	± 1.2	± 6.0	± 3.7	± 0.6	± 6.0	± 4.8	± 1.0	± 0.5	± 5	± 0.5
<u>Co</u>	31.7	9.5	3.0	/	/	/	/	/	/	8.0	/	/
<u>Co</u>	± 5.3	± 4.1	± 0.4	/	/	/	/	/	/	± 0.4	/	/

* ΔB_i represents the shift in the hyperfine field at the i th neighbor satellite line from that at the main cobalt line in the alloy.

We notice that ΔB observed for the various neighboring satellite lines in the Co-V and the Co-Cr alloys is in reasonable agreement with the predictions of our model for all except the second neighbor satellite line under assumption b).

In the case of Co-Mn, however, a large discrepancy is observed if the satellite line observed at 209.5 MHz is assumed to be the nearest neighbor line. The calculated value under assumption a) (using the neutron diffraction experiment parameters) should be ~ 186 MHz. An effort was made to search for a satellite line in this frequency region but none could be detected. As a matter of fact no echo signal could be observed below 200 MHz. Assumption b) leads to unrealistic values of Δu_2 and so no calculations have been done under it or under assumption c) which is a combination of a) and b). It should be pointed out that the satellite line observed is quite close to the frequency predicted for the second neighbor satellite line. If such is the case, it is hard to explain why the nearest neighbor satellite line should not be observable. On the other hand if this satellite line is the nearest neighbor line, why the anomalous shift ΔB ? The answer to this question may lie in the following possibility: Mn is known to behave anomalously in Fe-Mn where the resonance frequency of Mn has a much different temperature dependence than that of the Fe host.⁴⁵ This has been explained by Jaccarino et al.⁴⁶ on the assumption that Mn has a localised moment and the resonance frequency is proportional to the thermal average of this moment taken over its levels in the exchange field of Fe. If such is the case in Co-Mn also, the contribution to the hyperfine field from nearest neighbors is not expected to follow the simple empirical relation being considered here.

The general agreement between the predicted and observed

values of hyperfine field shifts for Co-Cr and Co-V alloys confirm our identification of satellite lines observed as coming from first and third nearest neighbors to the impurity. One further notices that the assumptions a) and c) lead to better agreement with the experimental values than does the assumption b). The disagreement between calculated and observed values of ΔB_2 is particularly strong. This assumption thus seems to be the weakest of all three. The fact that the predicted values of ΔB_1 are smaller than the experimental values (though within error) may be due to the contribution from second and farther neighbors.

4.3 Nuclear Spin-Spin Relaxation Times

We tabulate below the data on nuclear spin-spin relaxation times at the various lines of NMR spectra in our alloys.

TABLE 2

Nuclear spin-spin relaxation times, T_2 (μs)[†]

FREQ. ALLOY	ν_0	ν_1	ν_2	ν_3
<u>Co</u> -Cr	52	125	172	272
<u>Co</u> -V	40	102	129	154
<u>Co</u> -Mn	30	92*	—	144

The above values of T_2 need to be compared with the value of 88 μ s observed in pure cobalt by Weger et al.¹⁷ The data are characterized by the following salient features:

- a) For each alloy system the value of T_2 at the main line is smaller than that in pure cobalt and it increases rapidly to a value greater than that in pure cobalt at ν_1 ; the position of the third neighbor satellite line. For all other satellite lines the value of T_2 increases slowly but monotonically as one goes farther away from the cobalt main line. Co-Cr is an exception in that T_2 at ν_3 is considerably higher than T_2 at ν_2 .
- b) The relaxation times decrease monotonically as one goes from Cr to V to Mn impurities.

At the main line shorter relaxation times can be easily understood by considering the impurities as destroying the phase coherence between the precessing nuclear magnetic moment vectors. This is in accordance with Stearn's finding for dilute alloys of Fe and the mechanism suggested by her might well be operative here. (See Section 2.3). In this mechanism impurities tend to act like pinning points in the domain walls. In general this decreases the enhancement factor and leads to considerable variation in the total energy of the sample depending on the domain wall position. Thus it becomes quite probable that the wall may not return to the same position after each rf pulse. This can cause each domain wall nucleus to be

* This measurement has been made at 215 MHz

+ Errors are less than 10 per cent.

in a slightly different field after each pulse leading to an apparent contribution to the T_2 relaxation mechanism. For the satellite lines, an increase in T_2 is expected for an interaction of the Suhl-Nakamura type since the broad distribution of hyperfine fields produced at cobalt nuclei due to alloying, as well as the inhomogeneities introduced, tend to detune the resonant frequencies of a pair of nuclear spins to such an extent as to inhibit mutual spin-flips and thus reduce the S-N relaxation rate leading to longer transverse relaxation time. The same mechanism explains the rather large T_2 observed at ν_3 in Co-Cr as follows: The satellite line ν_3 is sharp, has very little overlap with ν_2 , and is well-separated from it (compare with Co-V). Furthermore since there are fewer nuclei contributing to ν_3 , the spin-spin relaxation time is expected to be longer than at ν_2 . (In the Suhl-Nakamura interaction the relaxation rate is proportional to the concentration of the active isotope.) Thus we have a qualitative explanation for the long T_2 observed at ν_3 in Co-Cr.

As regards the relative spin-spin relaxation rates in the different alloys, we believe that Stearn's mechanism can explain the observed behavior as follows: The Cr, V, and Mn impurities in cobalt have moments of $+0.45 \mu_B$, $0 \mu_B$, and $-0.97 \mu_B$ respectively.⁸ This should cause increasing pinning of domain walls in going from Cr to V to Mn and lead to increased relaxation in going from Co-Cr to Co-V to Co-Mn as observed. A further mechanism which is expected to cause faster relaxation for Mn and V alloys than for Cr is the nuclear spin-spin interactions be-

tween the host and the impurity. This is due to the fact that the natural abundance of the only non-zero spin isotope of Cr is 9.54% (Cr^{53} , $I=3/2$) whereas both Mn and V are 100% non-zero spin isotopes Mn^{55} ($I=5/2$) and V^{51} ($I=7/2$) respectively.

To sum up, the data on nuclear spin-spin relaxation in these alloys finds a qualitative explanation in terms of the Suhl-Nakamura interaction weakened by inhomogeneities in the internal fields, an apparent T_2 relaxation mechanism due to the presence of impurities which produce pinning points in the domain walls, and the nuclear spin-spin interaction between the host and the impurity.

4.4 Echo Envelope Modulation Effect

Our interest in this part of the work was aroused by the observation of a modulation of the echo envelope in Co-Cr alloy at 172.5 MHz. A sketch of the multiple exposure photograph of the same is shown in Fig. 8. The modulation period is 5.5 ± 0.5 μ sec which corresponds to a modulation frequency of 182 ± 17 KHz.

In section 2.4 we mentioned three mechanisms which could cause echo modulation in the case of cobalt alloys. Two of these pertain to indirect nuclear spin-spin interaction and the third one to the quadrupolar interaction of the nuclear quadrupole moment of cobalt nucleus interacting with the electric field gradient produced by broken symmetry around it. Among the spin-spin interactions are the Ruderman-Kittel (R-K) type interaction, $J \underline{I}_1 \cdot \underline{I}_2$, which in the presence of large inhomogeneous broadening in ferromagnetic materials reduces to the

form $J I_1^2 I_2^2$ and a transverse type Suhl-Nakamura (S-N) interaction. The interaction energy for S-N interaction is 1-10 kHz in pure cobalt³¹ and is expected to be smaller in alloys. (The inhomogeneities in alloys tend to weaken the S-N interaction.) Thus the modulation observed could not have been caused by S-N interaction. The R-K coupling constant in cobalt is not expected to be much greater than 1 kHz²⁹ and is not expected to be much different in the alloys studied. Thus the observed modulation frequency is too high to be explained by this mechanism either. Thus there is only one mechanism left, i.e. quadrupolar

Fig. 8. Echo envelope modulation in Co-Cr.

effects. We claim that the observed echo envelope modulation is due to quadrupolar effects. Since the echo envelope of only one component of the nearest neighbor line is modulated, it seems that only nuclei located in certain directions with respect to the impurity contribute to this modulation. A possible explanation for this is as follows: We recall from Section 2.4 that the quadrupolar Hamiltonian contains a term $(3 \cos^2 \theta - 1)$ where θ is the angle between B_{int} and the axis of symmetry of cylindrically symmetric electric field gradient. For nuclei in the domain wall the direction of local magnetisation changes continuously and so does $\cos \theta$. Thus an appropriate average of $(3 \cos^2 \theta - 1)$ over the wall nuclei should be considered. For nuclei contributing to the δ -function component of the line at 172.5 MHz in Co-Cr, we recall from Section 2.2 that $\cos \theta = 0$ regardless of the direction of local magnetisation. Thus $(3 \cos^2 \theta - 1) = -1$. For other nuclei averaging of $(3 \cos^2 \theta - 1)$ over the domain wall nuclei concerned might just smear out the echo envelope modulation effect.

In this picture it is understandable as to why no modulation is observed in Co-Mn. This is because the doublet is not resolved and the modulation depth thus would be 1/6th that in case of Co-Cr for the same signal at the satellite line. The signal in turn is smaller by a factor of six leading to an expected modulation of 1/36th that in Co-Cr. Little wonder that it is not observed.

In the case of Co-V it is not so obvious as to why no modulation is observed at 176 MHz. The echo signal in this case is

approximately one third of that observed for Co-Cr. (This is because of the metallurgical difficulties encountered with this alloy. The reader will recall from Section 3.1 that the satellite line signal in Co-V was found to decrease if the sample was annealed for a longer time or at a higher temperature.) Thus the echo envelope modulation depth would already be cut down to 1/3rd of the value of Co-Cr. This coupled with the nuclear spin-spin interaction between Co and V, which is at least ten times stronger than Co-Cr interaction may account for the fact that no echo modulation was observed for the Co-V system.

From the discussion above it seems that echo envelope modulation may be more easily observable on NMR signal from the domains where the direction of magnetisation for all nuclei is the same. For observing NMR from nuclei in the domains much higher rf power is needed. This was obtained by using an incoherent pulsed oscillator to see if the modulation depth was improved but without success.

To conclude, the modulation of echo envelope observed at 172.5 MHz in Co-Cr alloy is due to the interaction of quadrupole moment of cobalt nuclei with the electric field gradient created by the presence of an impurity atom in its nearest neighbor position which destroys the cubic symmetry. Only cobalt atoms in certain directions with respect to the impurity contribute to this modulation effect. Strong interactions between host and impurity nuclear spins may tend to destroy this modulation effect. Experiments should be done on Co-Ti to see if this effect is observable. (Ti like Cr has a low natural

abundance of non-zero nuclear spin isotopes and should enable a verification or rejection of this idea.)

Conclusions

Satellite lines have been observed in the NMR spin echo spectra of Co in Co-V, Co-Cr, and Co-Mn alloys. In the case of both Co-V and Co-Cr nearest neighbor and third nearest neighbor lines have been identified. The nearest neighbor satellite line is found to be split into two components due to dipolar and pseudo-dipolar interactions as predicted by the Murray-Marshall theory of NMR in dilute ferromagnetic alloys. In the case of Co-Mn only one clearly resolved satellite line has been observed which we assume to be the nearest neighbor line. The splitting in the case of Co-V and Co-Cr has been used to estimate the pseudo-dipolar moment of V and Cr impurities in Co. The absence of any splitting in the case of Co-Mn gives us an upper limit to the pseudo-dipolar moment. The empirical relation of Streever and Uriano and Kobayashi et al. has been used to calculate the frequency shifts for various satellite lines in these alloys. The results are in reasonable agreement with the observed values for Co-V and Co-Cr but a large discrepancy is found in the case of Co-Mn.

Spin-spin relaxation times measured for cobalt nuclei in these alloys indicate that both the Suhl-Nakamura interaction and a pinning effect in the domain walls due to the existence of impurities, as suggested by Stearns, seem to be operative. However, no conclusions can be drawn about the relative contributions of the two processes to the total spin-spin relaxation.

A modulation of the spin echo envelope has been observed for one component of the nearest neighbor line in the Co-Cr

alloy. This is shown to be of quadrupolar origin resulting from the broken symmetry of the lattice. That no modulation is observed for corresponding satellite line in the Co-V system may be due to the large nuclear spin-spin interaction in this alloy.

The work reported in this thesis strongly suggests the needs for two experiments:

- i) Measurements of the temperature dependence of the satellite line as well as that of Mn resonance in the Co-Mn alloy system.
- ii) Measurements similar to the present one on the Co-Ti alloy system to look for the echo modulation effect.

Experiment i) should throw some light on the anomalous behavior of Mn in Co as indicated by our results. Experiment ii) should confirm or reject our conjecture that nuclear spin-spin interactions between the host and impurity have some bearing on the observation of the echo modulation effect.

Appendix A

Filing Machine for NMR Samples

A sketch of our filing machine is shown in Fig. 9. A disc cutter (C), Disc 3 manufactured by Severance tool company, Saginaw, Michigan, is mounted at the end of a brass tube which is attached onto the reducer shaft of a speed reducer motor (Bodine type NSH-12R Model 301), the speed of which is controlled by using a speed controller (Model SH-14, Minarik Electric Company, Los Angeles California). The sample in the form of a cylindrical ingot is mounted on a sample holder by a set of three Allen screws. The sample holder itself is screwed onto a brass plate (A) which can rotate about a vertical shaft which goes through the plate (A) with 1/1000" clearance and press fits into a fixed brass plate (B) as indicated in the diagram. The brass plate (B) is kept fixed by the use of a right angle aluminum piece which is screwed onto it on one side and onto the base plane on the other. The sample is forced against the disc cutter with a constant force by connecting to the free end of the brass plate (A) a string which goes over a pulley and has suitable weights hung at its end. The entire set-up is mounted on a wooden base which is screwed onto a sturdy table to dampen vibrations. The filings are collected in a tray which can be slid under the cutter.

The machine is much simpler and more economical than other such machines reported in the literature.⁴⁷⁻⁴⁹

Fig. 9 A PERSPECTIVE DRAWING OF THE FILING MACHINE

Appendix B

Supplies for Tunnel Diode NMR Spectrometer

- a) Tunnel Diode Bias Supply: A circuit diagram of the tunnel diode bias supply is shown in Fig. 10(a). The use of a Zener diode (MCR 2225, 6.8V) and a simple voltage divider enables a voltage of ~ 0.1 volt to be obtained at the variable terminal of a 1 K, 10 turn potentiometer. This reference voltage is transformed to a lower impedance yielding a constant voltage source by the use of an operational amplifier (709) which also serves to amplify the signal from the oscillator.
- b) Varactor Biasing: The arrangement for applying a variable dc bias voltage for tuning and a superimposed ac for frequency modulation is shown in Fig. 10(b). The dc voltage is derived from a 0-160 V power supply (Hewlett Packard, Model 6207A) while the ac is obtained from the reference terminals of a lock-in amplifier (PAR, Model JB-5). Their ratio is kept constant through the use of a double potentiometer in order to prevent excessive modulation at low dc bias voltages. The two voltages are added in a simple adder circuit before application to the varactor.

Fig. 10. Supplies for the Tunnel Diode NMR Spectrometer
a) Tunnel diode bias supply
b) Varactor biasing arrangement

Appendix C

The Multivibrator Circuit

The multivibrator circuit needed for taking multiple exposure pictures of the spin echo envelope is shown in Fig. 11. The voltages of ± 6 volts required are obtained from standard dry batteries. The use of two instead of one transistor in each stage was found to be necessary to prevent the change of state on the fall of the trigger pulse.

Fig. 11. The Multivibrator Circuit

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