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THE EFFECT OF A METAL FILM ON THE SURFACE BOUNDARY CONDITIONS OF YTTRIUM IRON GARNET THIN FILMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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* * * * *

The Ohio State University

1980

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For my husband, Ira, and my daughter, Sarah.
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PUBLICATIONS


PRESENTATIONS


# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>VITA</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THEORY OF MAGNETISM IN THIN FILMS</td>
<td>5</td>
</tr>
<tr>
<td>A. Origin of Magnetism</td>
<td>5</td>
</tr>
<tr>
<td>B. Molecular Field Theory</td>
<td>10</td>
</tr>
<tr>
<td>C. Spin-wave Excitations</td>
<td>12</td>
</tr>
<tr>
<td>1. Equation of Motion</td>
<td>12</td>
</tr>
<tr>
<td>2. Dispersion Relation</td>
<td>15</td>
</tr>
<tr>
<td>3. Contributions to the Energy</td>
<td>20</td>
</tr>
<tr>
<td>(a) Zeeman energy</td>
<td>20</td>
</tr>
<tr>
<td>(b) Demagnetizing energy</td>
<td>20</td>
</tr>
<tr>
<td>(c) Uniaxial anistropy energy</td>
<td>22</td>
</tr>
<tr>
<td>(d) Crystalline anisotropy energy</td>
<td>23</td>
</tr>
<tr>
<td>4. Equilibrium Orientation</td>
<td>24</td>
</tr>
<tr>
<td>5. Boundary Conditions</td>
<td>25</td>
</tr>
<tr>
<td>6. Non-parallel Ground State</td>
<td>27</td>
</tr>
<tr>
<td>7. Critical Angle</td>
<td>31</td>
</tr>
<tr>
<td>III. MAGNETISM OF THE GARNETS</td>
<td>37</td>
</tr>
<tr>
<td>A. Crystal Structure</td>
<td>37</td>
</tr>
<tr>
<td>B. Superexchange</td>
<td>40</td>
</tr>
<tr>
<td>C. Ferrimagnetism</td>
<td>43</td>
</tr>
</tbody>
</table>
## IV. PROPERTIES OF THE METALS

A. Metal Cation Substitution into YIG .......................... 52  
B. Magnetic Structure of Cr ..................................... 53  
C. Band Structures .................................................. 56  
   1. Chromium ...................................................... 56  
   2. Vanadium ...................................................... 63  
D. Surface Magnetization .......................................... 63

## V. EXPERIMENTAL PROCEDURE .................................. 68

A. Sample Preparation ............................................. 68 
B. Spectrometer ..................................................... 70

## VI. SUBSTRATE SURFACE .......................................... 76

A. Magnetization Profile .......................................... 77 
B. Energy Profile .................................................... 84 
C. Effective Anistropy .............................................. 89 
D. Impurity Inclusions .............................................. 92

## VII. RESULTS ..................................................... 95

A. Control YIG ....................................................... 95 
B. Aluminum on YIG .................................................. 104 
C. Chromium on YIG .................................................. 114 
D. Vanadium on YIG .................................................. 121 
E. Summary ........................................................... 131

## BIBLIOGRAPHY .................................................... 135
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Characteristics of $\text{Y}_3\text{Fe}<em>5\text{O}</em>{12}$ Sample ADD-9 at Room Temperature</td>
<td>69</td>
</tr>
<tr>
<td>2. Properties of the Metals</td>
<td>69</td>
</tr>
<tr>
<td>3. The Isotropic and Uniaxial Contributions to the Free Surface Anisotropy at Room Temperature</td>
<td>132</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Diagrammatic representation of a spin vector precessing in a magnetic field</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Diagrammatic representation of two spin vectors giving total spin $S = 0$</td>
<td>9</td>
</tr>
<tr>
<td>3.</td>
<td>Diagrammatic representation of two spin vectors giving the three spin states of total spin $S = 1$</td>
<td>9</td>
</tr>
<tr>
<td>4.</td>
<td>Reduced magnetization versus reduced temperature for $S = 5/2$ and $S = 7/2$</td>
<td>13</td>
</tr>
<tr>
<td>5.</td>
<td>A travelling spin wave in which the precession phase changes from site to site</td>
<td>16</td>
</tr>
<tr>
<td>6.</td>
<td>A standing spin wave in which the amplitude of the precession changes from site to site</td>
<td>16</td>
</tr>
<tr>
<td>7.</td>
<td>Coordinate system of a thin magnetic film used in the continuum model</td>
<td>17</td>
</tr>
<tr>
<td>8.</td>
<td>The angle dependence of the surface parameter for a uniaxial surface anisotropy and a bulk anisotropy as described in Section C-3. Curve 1 is for the case of a parallel ground state and curve 2 is for the case of a non-parallel ground state</td>
<td>32</td>
</tr>
<tr>
<td>9.</td>
<td>The first two spin wave modes for symmetric and nonsymmetric boundary conditions. The surface parameter $A$ refers to layer 0 and surface parameter $B$ refers to layer L</td>
<td>34</td>
</tr>
<tr>
<td>10.</td>
<td>Array of cations in two octants of a garnet unit cell (after Pauthenet, 1958)</td>
<td>38</td>
</tr>
<tr>
<td>11.</td>
<td>The oxygen coordination of cations in YIG (after Gilleo, 1958)</td>
<td>39</td>
</tr>
<tr>
<td>12.</td>
<td>Schematic representation of a possible ground state in the superexchange of two Fe$^{3+}$ via O$^{2-}$</td>
<td>41</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>13</td>
<td>Schematic representation of the two spin possibilities of an excited state in the superexchange process</td>
<td>41</td>
</tr>
<tr>
<td>14</td>
<td>The temperature dependence of the sublattice magnetizations in GdIG (after Pauthenet, 1958)</td>
<td>46</td>
</tr>
<tr>
<td>15</td>
<td>The temperature dependence of the total magnetization of GdIG (after Pauthenet, 1958)</td>
<td>47</td>
</tr>
<tr>
<td>16</td>
<td>The temperature dependence of the magnetization of Gd$<em>X$Y$</em>{3-X}$Fe$<em>5$O$</em>{12}$ for six values of X (after von Aulock, 1965)</td>
<td>48</td>
</tr>
<tr>
<td>17</td>
<td>The temperature dependence of the effective g-factor of GdIG (after Rodrigue, 1960)</td>
<td>49</td>
</tr>
<tr>
<td>18</td>
<td>The temperature dependence of the magnetization of (Y$_{3-X}$Ca$_X$)$_2$(Fe$_3$-XGe$<em>X$)$</em>{12}$ for six values of X. Negative magnetization refers to X greater than the compensation value (after Krahn, 1978)</td>
<td>50</td>
</tr>
<tr>
<td>19</td>
<td>The variation of the effective g-factor at room temperature with substitution in (Y$_{3-X}$Ca$_X$)$_2$(Fe$_3$-XGe$<em>X$)$</em>{12}$ (after Gerhardstein, 1977)</td>
<td>51</td>
</tr>
<tr>
<td>20</td>
<td>Magnetic phase diagram for perfect, single crystal chromium (after Bacon and Cowlam, 1969)</td>
<td>57</td>
</tr>
<tr>
<td>21</td>
<td>Magnetic phase diagram for powdered chromium (after Bacon and Cowlam, 1969)</td>
<td>57</td>
</tr>
<tr>
<td>22</td>
<td>The first Brillouin zone for paramagnetic, body-centered cubic chromium.</td>
<td>58</td>
</tr>
<tr>
<td>23</td>
<td>The intersection of the Fermi surface with 1/48 Brillouin zone face for paramagnetic chromium (after Asano and Yamashita, 1967)</td>
<td>60</td>
</tr>
<tr>
<td>24</td>
<td>The intersection of the Fermi surface with 1/48 Brillouin zone face for antiferromagnetic chromium (after Asano and Yamashita, 1967)</td>
<td>61</td>
</tr>
<tr>
<td>25</td>
<td>The nesting of the hole surface about H into the electron surface about T, with the hole surface shifted by $\pm 0.04 (2\pi/c)$ (after Lomer, 1962)</td>
<td>62</td>
</tr>
</tbody>
</table>
26. Energy levels in vanadium as a function of lattice parameter. Magnetization begins just below 7.0 a.u. (after Hattox, et al. (1973)) ........................................... 64

27. Block diagram of the microwave resonance spectrometer ........................................... 71

28. The microwave magnetic field and the sample in the resonant cavities ........................................... 73

29. Schematic diagram showing how the loss of a magnetic ion in the "d" sublattice results in spin canting in the "a" sublattice and lowers the average value of $J_{aa}$ and $J_{ad}$ ................................................. 80

30. The sublattice magnetizations across the diffusion region for $T = 300K$ ........................................... 82

31. The total magnetization across the diffusion region for $T = 300K, 150K, 50K, 10K$ and $1.4K$ ............... 83

32. $V_{||}$ and $V_{\perp}$ for $T = 10K$ and $1.4K$ and a diffusion width of 25 nm ............................. 87

33. $V_{||}$ (normalized to $H_{||} + 2\gamma M$) for $T = 1.4K$ and two diffusion widths. The dotted curve is the best fit Morse potential for $W = 50$ nm. The value of $\beta$ corresponds to a full-width-at-half-minimum value of 3.1 nm .......................... 88

34. The anisotropy constant across the diffusion region as a function of temperature and diffusion width .................. 91

35. The perpendicular resonance spectrum of the control sample at 23.2 GHz and room temperature .............. 96

36. The linewidth at parallel resonance as a function of temperature for the control sample .................. 99

37. The linewidth at perpendicular resonance as a function of temperature for the control sample .................. 99

38. The spacing between the first two modes as a function of temperature for the control sample .................. 100

39. The parallel resonance spectrum of the control sample at 9.2 GHz and $T = 1.4K$ ............................. 101

x
40. The first three body modes and a bound state (solid curves) in a film with a Morse potential (dotted curve) at the substrate surface. The potential parameters are $A = 170$ Oe, $\beta = 7 \times 10^5$ cm$^{-1}$ and $y_e = 5.6 \times 10^{-5}$ cm. The amplitudes of the modes are arbitrary .................................. 103

41. The parallel resonance spectrum at 9.2 GHz and $T = 300$K for an Al/YIG sample which was annealed for 1 hr at 500°C in a nitrogen atmosphere ......................... 105

42. The linewidth at parallel resonance as a function of temperature for Al/YIG (1 hr anneal) sample .................... 106

43. The spacing between the second mode and the first and third modes as a function of temperature for the Al/YIG (1 hr anneal) sample ....................... 106

44. The ratio of the room temperature intensities of the second mode to the first mode as a function of total time etched in phosphoric acid at 84°C for Al/YIG (1 hr anneal) sample ......................... 108

45. The separation of the first two modes as a function of total time etched in phosphoric acid at 84°C for an Al/YIG (1 hr anneal) sample ....................... 109

46. A schematic representation of the magnetic potential across the film thickness (0.56 μm). The substrate surface is to the right. The depth of the well is 5.2 Oe and its width is 0.21 μm. The amplitudes of the modes are arbitrary .................................. 112

47. The perpendicular resonance spectrum at 9.2 GHz and $T = 300$K for a Cr/YIG sample ......................... 115

48. The temperature dependence of the relative intensities of the first two modes for Cr/YIG sample #31 ............ 116

49. The separation of the first two modes in perpendicular resonance as a function of temperature for Cr/YIG .......... 117

50. The temperature dependence of the relative intensities of the first four modes for Cr/YIG sample #26 ............ 119

51. A diagrammatic representation of the effect of Cr spins on the resonance modes of YIG ......................... 120
<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.</td>
<td>The perpendicular resonance spectrum at 9.2 GHz and T = 300K for a V/YIG sample</td>
<td>122</td>
</tr>
<tr>
<td>53.</td>
<td>The temperature dependence of the critical angle for V/YIG</td>
<td>123</td>
</tr>
<tr>
<td>54.</td>
<td>The spacing between the first two modes as a function of temperature for V/YIG</td>
<td>123</td>
</tr>
<tr>
<td>55.</td>
<td>The perpendicular resonance spectrum at 9.5 GHz and T = 20K for V/YIG</td>
<td>125</td>
</tr>
<tr>
<td>56.</td>
<td>The spacing between the first two modes in perpendicular resonance for T ≤ 50K for the control, Cr/YIG and V/YIG samples</td>
<td>126</td>
</tr>
<tr>
<td>57.</td>
<td>Best-fit curves of the relative intensities of the first two modes for the control and V/YIG samples as a function of temperature</td>
<td>127</td>
</tr>
<tr>
<td>58.</td>
<td>The free surface anisotropy constant for the control and V/YIG samples as a function of temperature</td>
<td>127</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Yttrium iron garnet is one of an important class of materials, the oxide magnetic insulators which include the garnets, spinels and hexagonal ferrites. The uniqueness of these ferrimagnets lies in the ease with which highly perfect single crystals can be grown. The method of choice, liquid-phase epitaxy, can be used for growing bulk (Remeika, 1956) or thin film (Linares, 1968) single crystals and lends itself to growing a large variety of materials by cation substitution in the basic oxide lattice. Thus the magnetic and physical properties of the oxide can be readily tailored.

The variety and availability of the magnetic garnets has made them enormously important in both research and industry. The garnets first found industrial application as microwave circuit devices such as isolators, circulators and gyrators (Standley, 1962). More recently, they have been used as binary storage devices (Bobek, 1967).

The garnets are valuable for experimental study because they are magnetic insulators with low dielectric loss. The magnetic moment per ion is localized to a lattice site and there are no conduction electrons or skin-depth effects to complicate analysis. In yttrium iron garnet (YIG) the Fe$^{3+}$ is an S-state ion, and there is no spin-orbit coupling (to first order) and hence a very narrow (<0.5 Oe) resonance linewidth. Relaxation mechanisms are found to depend principally on the rare-earth ion impurity concentration, which provides spin-orbit-
lattice coupling, and mechanical surface imperfections, which act as spin-wave scattering centers (Fletcher, et al., 1960). Thus, YIG is ideal for the investigation of spin-wave resonance theories.

The possibility of the excitation of spin waves in a ferromagnet by a uniform rf field was first proposed by Kittel, who postulated a surface anisotropy which acts to pin down surface spins (Kittel, 1958). The boundary condition implied is \( m|_{O,L} = 0 \); the resulting spin waves are sinusoidal, and in the long wavelength limit, the wavevector \( k = p\pi/L \), with \( L \) the number of layers in the film and \( p \) an integer. Pincus generalized the spin wave boundary condition by including a term proportional to the gradient of the magnetization with respect to the film normal, i.e., \( (am + b\nabla_m)|_{O,L} = 0 \) (Pincus, 1960). The constants of proportionality were identified by Soohoo with the surface anisotropy energy \( a \) and the exchange energy \( b \) (Soohoo, 1963).

Sokolov and Tavger and, independently, Wolf extended the theory by admitting the possibility of hyperbolic solutions to the equations of motion, giving rise to the surface modes with maximum amplitude at the film surface (Sokolov and Tavger, 1968; Wolf, 1962). In a series of papers, Puszkarski demonstrated the existence of an exchange-dominated surface mode and predicted the critical angle dependence of that mode (Puszkarski, 1970; Wigen and Puszkarski, 1976).

All these descriptions of spin wave excitations assume that the ground state is one in which the spins lie parallel in a direction determined by the bulk magnetic properties. However, the presence of
a surface anisotropy results in a ground state in which the surface spins are canted at an angle with respect to the bulk spins (Rado and Weertman, 1959). The influence of this nonparallel ground state on the boundary conditions has been investigated by Stakelon, using the continuum model (Stakelon, 1978) and by Harada and by Levy using the quantum theory (Harada, et al., 1977; Levy and Hung, 1978).

The problem facing the experimenter is to define the boundary conditions in terms of the actual physical conditions at the film interfaces. The major surface anisotropies in as-grown films of YIG occur at the YIG-substrate interface, and these have been studied in detail (Yu, et al., 1976; Yen, et al., 1979; Vittoria and Schelleng, 1977).

The purpose of the present study is to systematically alter the magnetic conditions at the free surface of a thin film of YIG and to study the resulting change in boundary conditions using ferromagnetic resonance. A thin film (about 50 to 100 nm) of the metals aluminum, chromium and vanadium evaporated onto the surface of the garnet was used to change the resonance boundary conditions. Once the details of the spectrum of the as-grown garnet had been studied, the response of the system to the presence of the metal layer could be determined. The resonance spectrum of the garnet could then be used as a probe to monitor magnetic transitions in the metal films.

Chapter II reviews the pertinent theories of magnetism, including its quantum mechanical origin, molecular field theory and spin-wave theory. The dispersion relation and boundary conditions for spin-
wave excitations for thin films are derived using the continuum model. Included is a brief discussion of the effects of the non-parallel ground state and the presence of two surfaces.

The magnetic structure of the garnets is presented in Chapter III. The effects of substitution on magnetic properties is discussed in view of the conditions of the YIG-substrate interface. Chapter IV reviews the properties of the metals used, as cation substituents in a garnet and as free metals. A brief presentation of the complicated magnetic structure of chromium is given. Some recent theoretical and experimental results on the magnetic properties of metal surfaces is also provided.

The details of sample preparation and the microwave spectrometer are given in Chapter V. The results of studies on the physical condition of the YIG-substrate interface is the subject of Chapter VI. Finally, the results of this study of as-grown YIG and the metal-evaporated YIG samples along with a discussion of the altered magnetic boundaries is presented in Chapter VII.
II. THEORY OF MAGNETISM IN THIN FILMS

A. Origin of Magnetism

The forces which give rise to the phenomenon of ferromagnetism are the static Coulombic forces between electrons associated with neighboring atoms. The energy, $E$, of a two-electron system can be approximated by (Heisenberg, 1928)

$$E_\pm = \langle \psi_\pm | H | \psi_\pm \rangle,$$  \hspace{1cm} (II-1)

where

$$\psi_\pm(\vec{r}_1, \vec{r}_2) = N_\pm [U_n(\vec{r}_1)U_m(\vec{r}_2) \pm U_m(\vec{r}_1)U_n(\vec{r}_2)].$$  \hspace{1cm} (II-2)

$N_\pm$ is the normalization constant and $U_n$ and $U_m$ are one-electron functions. The linear combination of functions is required by the Pauli exclusion principle. The complete Hamiltonian, $H$, includes the one-electron terms, $H_1$ and $H_2$, and the perturbation term $K_{12}$. The full expression for $E$ is then

$$E_\pm = E_n + E_m + 2N_\pm^2 (K_{12} \pm J),$$  \hspace{1cm} (II-3)

where

$$E_n = \langle U_n(\vec{r}_1) | H_1 | U_n(\vec{r}_1) \rangle,$$  \hspace{1cm} (II-4a)

$$E_m = \langle U_m(\vec{r}_2) | H_2 | U_m(\vec{r}_2) \rangle,$$  \hspace{1cm} (II-4b)

$$K = \langle U_n(\vec{r}_1)U_m(\vec{r}_2) | K_{12} | U_n(\vec{r}_1)U_m(\vec{r}_2) \rangle,$$  \hspace{1cm} (II-4c)

$$J = \langle U_n(\vec{r}_1)U_m(\vec{r}_2) | J_{12} | U_m(\vec{r}_1)U_n(\vec{r}_2) \rangle.$$  \hspace{1cm} (II-4d)
$$S_z = \pm \frac{1}{2} \hbar, \quad \langle S_x \rangle = \langle S_y \rangle = 0$$

$$S_z^2 = S_x^2 = S_y^2 = \frac{1}{4} \hbar^2$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{4} \hbar^2$$

$$|S| = \sqrt{\frac{3}{4}} \hbar$$

Figure 1. Diagrammatic representation of a spin vector precessing in a magnetic field.
The Coulomb integral $K$ is interpreted as an electrostatic interaction of charge clouds, while $J$, known as the exchange integral, introduces additional correlations in the electrons' movements based on the symmetry requirements of the Fermi particles.

The symmetry requirement is that the total wavefunction must be antisymmetric with respect to exchange of the particles. There are two possibilities:

$$\Psi = \psi_A (\vec{r}_1, \vec{r}_2) \chi_S (\sigma_1, \sigma_2), \quad (II-5a)$$
$$\Psi = \psi_S (\vec{r}_1, \vec{r}_2) \chi_A (\sigma_1, \sigma_2) \quad (II-5b)$$

where the $\chi$'s and $\sigma$'s are the functions and arguments of a property of electrons known as spin angular momentum. This angular momentum has a fixed value of $|s| = \sqrt{3/4} \hbar$ per electron which is written in terms of a spin quantum number $s$ as $\sqrt{s(s+1)} \hbar$ in analogy with electronic orbital angular momentum. Then, for an electron, $s = 1/2$.

The component of $s$ along the direction of a magnetic field is $s_z = \pm 1/2 \hbar$, while the transverse components $< s_x >$ and $< s_y >$ are zero, from the Heisenberg uncertainty principle. Figure 1 summarizes these facts. Traditionally, the spin function for which $s_z = + 1/2 \hbar$ (up spin) is given as $\chi_\alpha (\sigma)$ and that for $s_z = -1/2 \hbar$ (down spin) is $\chi_\beta (\sigma)$.

In the one-electron approximation, there is one symmetric orbital wavefunction $\psi_+ (\vec{r}_1, \vec{r}_2)$ and one antisymmetric orbital wavefunction $\psi_- (\vec{r}_1, \vec{r}_2)$. For the spin wavefunctions, there exist:

$$\chi_A (\sigma_1, \sigma_2) = 1/\sqrt{2} \left[ \chi_\alpha (\sigma_1) \chi_\beta (\sigma_2) - \chi_\beta (\sigma_1) \chi_\alpha (\sigma_2) \right]; \quad (II-6a)$$
\( \chi^I_s(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}[\chi_\alpha(\sigma_1)\chi_\beta(\sigma_2) + \chi_\beta(\sigma_1)\chi_\alpha(\sigma_2)], \) (II-6b)

\( \chi^{II}_s(\sigma_1, \sigma_2) = \chi_\alpha(\sigma_1)\chi_\alpha(\sigma_2), \) (II-6c)

\( \chi^{III}_s(\sigma_1, \sigma_2) = \chi_\beta(\sigma_1)\chi_\beta(\sigma_2). \) (II-6d)

Figure 2 and Figure 3 illustrate these spin possibilities. The total spin quantum number, \( S \), is given by

\[
|S|^2 = S(S+1) = S^2 + S_1^2 + S_2^2 = (s_1 + s_2)^2 + (s_1 + s_2)^2 + (s_1 + s_2)^2
\]

A singlet \((S = 0)\) antisymmetric spin state is associated with a symmetric orbital wavefunction, and a triplet \((S = 1)\) symmetric state is associated with an antisymmetric orbital wavefunction. The connection between the exchange integral \( J \) and the spin is thus established.

From the energy, Eq. (II-3), if \( J \) is positive, the symmetric spin state, with a parallel spin alignment is the ground state; if \( J \) is negative, the singlet state with antiparallel spin alignment is preferred.

The Hamiltonian representing exchange effects (Ashcroft and Mermin, 1976) is written in terms of spins as

\[
H_{\text{ex}} = -J_{ij}(1/2 + 2(S_i^z S_j^z)/\hbar^2). \tag{II-8}
\]

The difference in energy between the singlet and triplet states is, from Eq. (II-8)

\[
\Delta E = E_T - E_S = 2J_{ij}, \tag{II-9a}
\]

and from Eq. (II-3)

\[
\Delta E = E_- - E_+ = 2[K(N_+^2 - N_-^2) + J(N_+^2 N_-^2)]. \tag{II-9b}
\]
Figure 2. Diagrammatic representation of two spin vectors giving total spin $S = 0$.

Figure 3. Diagrammatic representation of two spin vectors giving the three spin states of total spin $S = 1$. 
If one-electron orbital wavefunctions are used, \( N_+ = N_- \) and \( J_{ij} = J \). When non-orthogonal wavefunctions are used, the entire right-hand-side of Eq. (II-9b) must be considered \( J_{ij}' \), the exchange constant.

In addition to this electrostatic interaction there exists the classic magnetic dipolar interaction between the spin moments. The Hamiltonian is

\[
H_{\text{mag}} = \frac{1}{r_{ij}^3} \left[ \frac{\hat{\mu}_i \cdot \hat{\mu}_j}{3} - \frac{3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_i \cdot \hat{r}_{ij})}{r_{ij}^3} \right] 
\]

(II-10)

with \( \hat{\mu}_i = \frac{-e}{m_c} \hat{S}_i \).

The exchange interaction is of short-range, falling off exponentially with spin separation (with the orbital wavefunction) in an insulator. The magnetic dipolar interaction falls off only as the inverse cube of the separation. The dipolar energy can be substantially reduced by dividing a sample of a ferromagnetic material into domains in which the magnetizations are in different directions. While the exchange interaction results in the phenomenon of ferromagnetism, the magnetic dipolar interaction is the cause of magnetic domains.

B. Molecular Field Theory

The first theory to successfully predict the behavior of magnetically ordered materials was proposed by Weiss (Weiss, 1907). He reduced the problem of ferromagnetism to that of paramagnetism by assuming that each spin dipole moment was influenced by an internal molecular magnetic field of unknown quantity (and origin). The total field acting on each spin is
\[ H = H_{\text{app}} + \lambda M_s \]  \hspace{1cm} (II-11)

where \( M_s \) is the spontaneous magnetization due to the molecular field and \( \lambda \) is the molecular field coefficient. The spontaneous magnetization can be calculated for a paramagnetic system using statistical theory (Kittel, 1976)

\[ M_s = M_0 B_s \left( \mu_m H/kT \right), \]  \hspace{1cm} (II-12)

where \( \mu_m \) is magnetic dipole moment, \( k \) is Boltzmann's constant and \( T \) is the absolute temperature. The expression \( B_s(x) \) represents the Brillouin functions given by

\[ B_s(x) = \frac{2S+1}{2S} \coth \left( \frac{2S+1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} x \right). \]

The maximum value of the magnetization, \( M_0 \), is achieved in infinite field or at zero temperature. Eq. (II-11) and Eq. (II-12) must be solved simultaneously for the spontaneous magnetization and the field.

This simple model agrees qualitatively with experiment. \( \mu_m \) can be regarded as an adjustable parameter.) It has the wrong limiting behavior as the Curie temperature is approached. The magnetization is predicted to approach zero as \((T - T_c)^{1/2}\) as \( T \to T_c \) from below. Experimentally, the exponent is found to be 1/3. The theory also fails to predict the Bloch \( T^{3/2} \) law that \( M_o - M \propto T^{3/2} \) as \( T \) approaches zero.

The value of the molecular field for a ferromagnetic material is very much greater than any realizable applied field, on the order of \( 10^7 \text{ Oe} \). (For this reason, \( H_{\text{app}} \) can be ignored when solving Eq. (II-11).) Heisenberg (Heisenberg, 1928) recognized that the strong interaction responsible for the molecular field was the exchange interaction. The spin magnetic moment is then given by
\[ \mu_m = -\frac{e}{mc} S = g\mu_BS, \quad (II-13) \]

where \( g \) is the spectroscopic splitting factor, \( \mu_B \) is the Bohr magneton and \( S \) is the total spin quantum number. Then

\[ M_0 = N\mu_m \quad (II-14) \]

where \( N \) is the density of spins.

The critical temperature \( T_c \) is the temperature at which \( M_s \) goes to zero and is given by the theory as

\[ T_c = \frac{S(S+1)}{3k} \lambda Ng^2 \mu_B^2. \quad (II-15) \]

The reduced magnetization \( M_s/M_0 \) can be written in terms of the reduced temperature \( T/T_c \):

\[ \frac{M_s}{M_0} = B_s \left( \frac{3S}{S+1} \frac{T_c}{T} \frac{M_s}{M_0} \right), \quad (II-16) \]

which for given values of \( S \) is a universal function. Figure 4 illustrates the temperature dependence of the spontaneous magnetization for values of \( S = 5/2 \) and \( S = 7/2 \) corresponding to Fe\(^{3+}\) and Gd\(^{3+}\), respectively.

C. Spin-wave Excitations

1. Equation of Motion

As seen in Section A of this chapter, the effect of Coulombic exchange can be represented by an interaction between spin vectors. For materials in which \( J_{ij} \) is positive, the exchange interaction leads to spontaneous magnetization. From observations of domain wall widths, it is found that the exchange interaction strongly resists a change in the direction of the magnetization from site to site (Jones and Middleton, 1974). For this reason, the equation of motion of a
Figure 4. Reduced magnetization versus reduced temperature for $S = 5/2$ and $S = 7/2$. 
configuration of discrete spin vectors can be transformed to that of a
spin or magnetization density field. This treatment is called the
microscopic continuum model.

For an array of spins in a crystal lattice, the Hamiltonian, in­
cluding Zeeman and exchange terms, is
\[ K = - g \mu_B \sum_i \vec{H}_i \cdot \vec{S}_i - 2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j, \] (II-17)
where \( \vec{H}_i \) accounts for all applied and internal fields. The spin \( \vec{S}_j \)
can be expanded in a Taylor Series about the spin \( \vec{S}_i \).
\[
\vec{S}_j = \vec{S}_i + [(\vec{r}_j - \vec{r}_i) \cdot \vec{V}] \vec{S}_i + 1/2 [(\vec{r}_j - \vec{r}_i) \cdot \vec{V}]^2 \vec{S}_i + \ldots \quad (II-18)
\]
The zeroeth-order term will be absorbed in the definition of the ground
state. Assuming nearest neighbor coupling \((J_{ij} = J, a \text{ constant})\) and a
cubic lattice, the first-order term will vanish by symmetry. The
second-order term is the first to contribute to the spin energy density.

The Hamiltonian becomes
\[ K = -g \mu_B \sum_i \vec{H}_i \cdot \vec{S}_i - 2Ja^2z \sum_i \vec{S}_i \cdot \nabla^2 \vec{S}_i, \] (II-19)
where \( a \) is the cubic lattice constant and \( z \) is the number of nearest
neighbors.

The equation of motion for the \( i \) th spin is (Schiff, 1968)
\[
i\hbar \frac{d\vec{S}_i}{dt} = [\vec{S}_i, \mathcal{K}]. \quad (II-20)
\]
Using the quantization relation
\[ \vec{S}_i \times \vec{S}_j = i\hbar \delta_{ij}, \quad (II-21)\]
an equation of motion for the magnetization can be derived by substi­
tuting from Section B
where \( \gamma \) is the gyromagnetic ratio, \( \gamma = \frac{g\mu_B}{\hbar} \), and \( G \) is the exchange stiffness constant which measures the strength of the exchange interaction.

\[
G = \frac{JzS^2}{a}\]

Eq. (II-23) is the classical equation for precession, so that a spin wave can be viewed as the precession of the spin or magnetization vector in the total field. Figure 5 represents travelling spin waves and Figure 6 standing spin waves. A travelling spin wave is one in which the phase of the precession of the spin vector changes from site to site. In a standing spin wave, the phase of the precession remains constant, but the amplitude of the precession varies.

2. Dispersion Relation

A simplification in the treatment of the equation of motion can be made by noting that the right-hand-side of Eq. (II-23) is the torque acting on the magnetization. The problem of evaluating the vector field \((\mathbf{H} + G\nabla^2\mathbf{M})\) is reduced to one of evaluating a scalar energy density by the relation

\[
\frac{1}{\gamma} \frac{d\mathbf{M}}{dt} = \mathbf{\tau} = \mathbf{\hat{r}} \times (-\mathbf{\nabla}E_T) = -\frac{\mathbf{M}}{M_0} \times \mathbf{\nabla}E_T. \tag{II-24}
\]

The coordinate system for a thin magnetic film is shown in Figure 7. The form of the energy density \(E_T\), will be discussed in the next part of this section. The exchange energy will be handled separately, so
Figure 5. A travelling spin wave in which the precession phase changes from site to site.

Figure 6. A standing spin wave in which the amplitude of the precession changes from site to site.
Figure 7. Coordinate system of a thin magnetic film used in the continuum model.
Also note that $E$ is a function of $\theta$ and $\phi$ only.

The desired solutions to Eq. (11-23) are of the form

$$\mathbf{M} = \mathbf{M}_o + \mathbf{m} = \mathbf{M}_o \hat{r} + m_\theta \hat{\theta} + m_\phi \hat{\phi}, \quad (11-25)$$

where $\mathbf{M}_o$ is the uniform magnetization and $\mathbf{m}$ is the deviation from $\mathbf{M}_o$. The unit vector $\hat{r}$ is in the direction of $\mathbf{M}_o$ and $\hat{\theta}$ and $\hat{\phi}$ are the azimuthal and polar Euler angle unit vectors. $|\mathbf{M}_o|$ is very much greater than $|\mathbf{m}|$.

The static equilibrium configuration of the spins is determined by solving the zeroth-order equation of motion with $\dot{\mathbf{M}} = \mathbf{M}_o$.

$$0 = -\frac{\mathbf{M}}{M_o} \times \nabla E - \frac{2G}{M_o^2} \mathbf{M} \times \nabla^2 \mathbf{M}$$

$$= E_\theta \hat{\phi} - \csc \theta E_\phi \hat{\theta}, \quad (II-26)$$

where $E_\theta (E_\phi)$ denotes the first derivative of $E$ with respect to $\theta (\phi)$. This relation implies that

$$E_\theta, E_\phi = 0 \quad (II-27)$$

The dynamic response of the magnetization can be evaluated by considering a contribution to the torque, $\delta \mathbf{T}$, due to the deviation of $\mathbf{M}$ from its equilibrium position.

$$\delta \mathbf{T} = -\delta \left( \frac{\mathbf{M}}{M_o} \times \nabla E \right) - \frac{2G}{M_o^2} \delta (\mathbf{M} \times \nabla^2 \mathbf{M}), \quad (II-28a)$$

$$\delta \left( \frac{\mathbf{M}}{M_o} \right) \times \nabla E = \frac{1}{M_o} (E_\phi \csc \theta m_\theta - E_\theta m_\phi) \hat{r}, \quad (II-28b)$$
\[ \frac{\dot{M}}{M_0} \times \delta \vec{V}_E = \frac{1}{M_0} \left[ -\left( E_\theta \cot \theta m_\theta + E_\phi \csc \theta m_\phi + E_\phi \csc^2 \theta m_\phi \right) \right. \]
\[ \left. - E_\phi \cot \theta \csc \theta m_\phi \right) \dot{\theta} \]
\[ + \left( E_\theta \theta m_\theta + E_\phi \csc \theta m_\phi - E_\phi \cot \theta \csc \theta m_\phi \right) \dot{\phi}, \]
\[ \delta (\dot{M} \times \nabla^2 \dot{m}) = (-\dot{M} \nabla^2 \dot{m}) \dot{\theta} + (M \nabla^2 \dot{m}) \dot{\phi}, \]
where only terms first order in \( m_\theta, m_\phi, \theta, \phi, \) and their spatial derivatives have been kept. To arrive at Eq. (II-28) the following relationships were used (Morse and Feshbach, 1953):
\[ m_\theta = M_0 \delta \theta \]
\[ m_\phi = M_0 \sin \theta \delta \phi, \]  
\[ \dot{\theta} = -\hat{r} \delta \theta + \hat{\phi} \cos \theta \delta \phi, \]
\[ \dot{\phi} = -\hat{r} \sin \theta \delta \theta - \hat{\theta} \cos \theta \delta \phi. \]
Substituting Eq. (II-27) and Eq. (II-28) into Eq. (II-25) leads to a set of coupled equations of motion.
\[ \frac{1}{\gamma} \frac{dm_\theta}{dt} = \csc \theta \left( \dot{E}_\theta \theta m_\theta + \dot{E}_\phi \csc \theta m_\phi \right) - \frac{2G}{M_0} \nabla^2 m_\theta, \]
\[ \frac{1}{\gamma} \frac{dm_\phi}{dt} = -\frac{1}{M_0} \left( \dot{E}_\theta \theta m_\theta + \dot{E}_\phi \csc \theta m_\phi \right) + \frac{2G}{M_0} \nabla^2 m_\theta. \]
The solutions are
\[ m_\theta = [\alpha_1 \sin k_1 \gamma + \beta_1 \cos k_1 \gamma + \gamma_1 e^{k_2 \gamma}] e^{-i \omega t}, \]
\[ m_\phi = [\alpha_2 \sin k_1 \gamma + \beta_2 \cos k_1 \gamma + \gamma_2 e^{k_2 \gamma}] e^{-i \omega t}. \]
The dispersion relation is given by
\[ k_{1,2}^2 = \left( \frac{\dot{E}_\theta \theta + \dot{E}_\phi \phi}{2} \right) + \left\{ \left( \frac{\dot{E}_\theta \theta - \dot{E}_\phi \phi}{2} \right)^2 + \Omega^2 + \left( \frac{\dot{E}_\phi \phi}{2} \right)^2 \right\}^{1/2}, \]
where \( \Omega = \omega / \gamma \) and \( E_\theta \theta = E_\theta \theta / 2G. \)
The two wavevectors correspond to different types of excited states. The wavevector \( k_2 \) is associated with an exponentially decaying mode that precesses in a sense opposite to that of the mode associated with \( k_1 \). The decay length of the \( k_2 \) mode for pure YIG at 9.2 GHz is 12.3 nm. The amount of energy absorbed by this mode in a film with thickness on the order of 1 \( \mu \)m is negligible and can be ignored.

The spin-wave excitations are those associated with the wavevector \( k_1 \). Note that the form of Eq. (11-32) allows both real and imaginary values for \( k_1 \), corresponding to body and surface spin waves (Puszkarski, 1970).

3. Contributions to the Energy

The interactions which contribute to the energy density which appears in the equation of motion will now be evaluated for a thin film of a cubic material.

(a) Zeeman energy

The Zeeman energy is the energy of interaction of the magnetization with the applied field. Referring to Figure 7

\[
E_Z = \mathbf{M} \cdot \mathbf{H}_{\text{app}} = -MH\sin\theta\cos(\phi - \phi_H). \tag{II-33}
\]

(b) Demagnetizing energy

The demagnetizing energy is the work which must be done to align a magnetic moment in the field generated by all other magnetic moments to reach the configuration of minimum energy. Application of an external field must overcome this internal alignment before the magnetic moments can be realigned parallel to the external field.
In a two-moment system, the magnetic interaction is given by Eq. (II-10). In a magnetically ordered material

\[ \hat{\mu}_1 = \pm \hat{\mu}_2, \quad |\hat{\mu}_1| = u. \]  

(II-34)

The dipole interaction energy becomes

\[ E_d = \frac{\mu^2}{r^3} (1 - 3 \cos^2 \beta), \]  

(II-35)

where \( \beta \) is the angle between \( \hat{\mu} \) and \( \hat{r} \). The minimum energy configuration occurs when the dipoles are aligned parallel to their connecting line.

If these moments are then rotated away from this minimum energy axis, there will be a restoring torque which can be expressed in terms of an effective field,

\[ \hat{T}_d = \hat{M}_d \times \hat{H}_d, \]  

(II-36)

where \( \hat{M}_d = 2\hat{u} \) is the magnetic moment of the dipole pair. Since \( \hat{H}_d \) is defined through the torque, neither its magnitude nor its direction is unique; any vector \( \lambda \hat{M}_d \) can be added to \( \hat{H}_d \) without changing the torque since \( \hat{M}_d \times \hat{M}_d \) is zero. The most convenient notation for \( \hat{H}_d \) is to express it in terms of \( \hat{M}_d \):

\[ \hat{H}_d = ([D] + \lambda [I]) \hat{M}_d, \]  

(II-37)

where \([I]\) is the unit matrix.

For the minimum energy configuration of two dipoles

\[ [D] = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D \end{bmatrix} \]

If \( \lambda = -D \) is chosen, then the directional behavior of \( \hat{H}_d \) is illustrated.

\[ \hat{T} = \hat{M}_d \times [D] \hat{M}_d = -\hat{M}_d \times [D'] \hat{M}_d, \]  

(II-38)
where

\[
[D'] = \begin{bmatrix}
D & 0 & 0 \\
0 & D & 0 \\
0 & 0 & 0
\end{bmatrix}.
\]

For a three-dimensional array of magnetic dipoles, the internal field \( \vec{H}_d \) can still be expressed as the product of a tensor and the total magnetic moment (von Aulock, 1965). The demagnetization tensor \([N]\) depends on the macroscopic shape of the sample. The demagnetization energy is

\[
E_D = \frac{1}{2} \vec{M} \cdot [N] \cdot \vec{M}.
\] (II-39)

For a thin film as shown in Figure 7,

\[
E_D = 2\pi M_y^2 = 2\pi M^2 \sin^2 \theta \sin^2 \phi.
\] (II-40)

Very simply, when a field is applied normal to the surface of a film, magnetic monopoles are induced on the surfaces which provide a field which opposes the applied field. When the applied field is parallel to the film plane, there is no demagnetizing field opposing it.

(c) Uniaxial anisotropy energy

There are two sources of uniaxial anisotropy in epitaxially-grown garnet films. The first is a growth-induced uniaxial anisotropy resulting from strong site preferences of rare-earth ion substituents into the "dodecahedral" site or the preference of Ga\(^{3+}\) for the smaller "d" site in mixed iron-gallium garnets (Geller, et al., 1964). For pure YIG, this substitution is important only at the substrate surface.

The second source of uniaxial anisotropy is a stress-induced one arising from lattice constant mismatch between the substrate and the magnetic film. The lattice constant of Czochralski-grown (melt pulled)
Gd$_3$Ga$_5$O$_{12}$ boule is 1.2384 nm. Since the lattice constant of Y$_3$Fe$_5$O$_{12}$ is 1.2376 nm, the magnetic film is in tension (Giess, et al., 1971). The axis of the anisotropy is perpendicular to the film plane, so that

$$E_u = K_u \sin^2 \theta \sin^2 \phi.$$  \hspace{1cm} (II-41)

In YIG, $K_u$ is small compared to $4\pi M$ and Eq. (II-41) is included in the demagnetization term. The value of $4\pi M$ measured by magnetic resonance includes the effect of uniaxial anisotropy.

(d) Crystalline anisotropy energy

Experimentally, it is found that the magnetization tends to lie along preferred crystallographic axes. Thus, there must exist a coupling between the spin system and the crystal lattice. The electric field of the lattice does not couple directly with the spin angular moments of the ions, but it does couple with orbital angular momentum. If there is appreciable spin-orbit coupling in the ion, there exists an indirect interaction between the spin and the crystalline electric field.

The crystalline anisotropy energy is the work required to make the magnetization lie along a certain direction compared to an "easy" direction. The form of the crystalline anisotropy energy is usually given as a power series of the direction cosines of the magnetization with the principle crystal axes (Akulov, 1929). For a cubic system, all odd-power terms and cross-terms of power $2n$ with $n$ odd will be zero. The second-order term will not contribute since $a_1^2 + a_2^2 + a_3^2 = 1$. The first contributing term is of fourth degree.
\[ E_c = K_1 \left( \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 \right) \]  \hspace{1cm} (II-42)

For a sample with a [100] axis along the film normal, the energy is

\[ E_c = K_1 \left[ \frac{11}{64} - \frac{\cos 2\theta}{16} - \frac{7 \cos 4\theta}{64} - \frac{3 \cos 4\phi}{64} + \frac{\cos 2\theta \cos 4\phi}{16} - \frac{\cos 4\theta \cos 4\phi}{64} \right]. \]  \hspace{1cm} (II-43)

Again, for pure YIG, this contribution to the energy will be small, since, ideally, the only magnetic ion is Fe\(^{3+}\) which has no orbital angular momentum. The small anisotropy which does exist is attributed to a distortion of the Fe\(^{3+}\) ion by the crystal field, which induces a small amount of orbital angular momentum which couples the spin to the crystal lattice.

4. Equilibrium Orientation

The equilibrium condition is given by Eq. (II-27). The equation

\[ E_\theta = 0 \] implies that the equilibrium value of \( \theta \) is \( \theta_o = \pi/2 \). Setting \( E_\theta = 0 \) with \( \theta = \theta_o \) yields the relation:

\[ -M H \sin (\phi - \phi_H) + 2 \pi M \sin 2\phi + 1/2 K_1 \sin 4\phi = 0. \]  \hspace{1cm} (II-44)

The dispersion relation can also be evaluated. It is easily seen that \( E_{\theta\phi} = 0 \). The angles \( \phi \) and \( \phi_H \) are now transformed to angles \( \zeta \) and \( \zeta_H \), which are the angles between \( \vec{M} \) and \( \vec{H} \) and the film normal:

\[ \zeta = \pi/2 - \phi, \quad \zeta_H = \pi/2 - \phi_H. \] The applied field is confined to a (001) plane. The dispersion relation becomes (Yu, et al., 1975)

\[ (\omega/\gamma)^2 = [\text{Hcos} (\zeta_H - \zeta) - 4\pi M \cos 2\zeta - q_1(\zeta) + Dk^2_{1}] \times [\text{Hcos}(\zeta_H - \zeta) - 4\pi M \cos^2 \zeta - q_2(\zeta) + Dk^2_{1}], \]  \hspace{1cm} (II-45)

where \( D \) is the dispersion constant, \( D = 2\gamma/M \).

The equilibrium orientation of the magnetization given in Eq. (II-44)
becomes
\[ 2\pi M \sin 2\zeta + H \sin (\zeta_H - \zeta) + g_3(\zeta) = 0. \]  
(II-46)

The crystalline anisotropy fields are given by
\[ g_1(\zeta) = -H_K \cos 4\zeta, \]  
(II-47a)
\[ g_3(\zeta) = -\frac{1}{4} H_K (3 + \cos 4\zeta), \]  
(II-47b)
\[ g_3(\zeta) = \frac{1}{4} H_K \sin 4\zeta, \]  
(II-47c)

where \( H_K = 2 |K_1| / M \). The fact that \( K_1 \) is negative for YIG has been accounted for.

The field of the uniform precession (\( k_1 = 0 \)) can be obtained from Eq. (II-45) and Eq. (II-46).
\[
H_U(\zeta) = \frac{2\pi M}{\cos(\zeta - \zeta_H)} \left\{ \frac{1 + 3\cos 2\zeta}{2} + \frac{H_K}{4\pi M} \left( \frac{3 + 5\cos 4\zeta}{4} \right) \right. \\
\left. + \left[ \left( \frac{\cos 2\zeta - 1}{2} + \frac{H_K}{4\pi M} \frac{3(\cos 4\zeta - 1)}{4} \right)^2 + \left( \frac{\omega/\gamma}{4\pi M} \right)^2 \right]^{1/2} \right\}.  
(II-48)

The magnetization angle \( \zeta \) can be evaluated as a function of magnet angle \( \zeta_H \) from Eq. (II-46).

5. Boundary Conditions

The spectrum of \( k_1 \) values will be determined by the physical conditions at the surfaces of the thin film. The surface torque generated from the surface energy density is
\[ \vec{\tau}^S = -\frac{\vec{M}}{M_0} \times \vec{V} E^S. \]  
(II-49)

At a surface, the first-order term in the Taylor expansion of Eq. (II-18) does not cancel by symmetry and must be included (Rado and Weertman, 1959).
\[ \mathbf{t}^s = \frac{2 G}{M_0^2} \mathbf{M} \times \frac{\partial \mathbf{m}}{\partial y} \]  

(II-50)

The surface exchange torque balances the surface anisotropy torque.

If the parallel ground state is assumed (one in which the surface spin vectors lie parallel to the bulk spin vectors), the surface torques have no effect on the equilibrium configuration. The dynamic response is obtained by the methods used for Eq. (II-28) and Eq. (II-29). The surface exchange torque has the form

\[
\delta t^s = \frac{2a}{M_0} \left( \frac{\partial m_\theta}{\partial y} \hat{\phi} - \frac{\partial m_\phi}{\partial y} \hat{\theta} \right)
\]  

(II-51)

Setting \( \theta = \pi/2 \), the boundary conditions become

\[
\begin{bmatrix}
\frac{\partial m_\theta}{\partial y} \\
\frac{\partial m_\phi}{\partial y}
\end{bmatrix} = \begin{bmatrix}
E_{\theta \theta}^s & E_{\theta \phi}^s \\
E_{\phi \theta}^s & E_{\phi \phi}^s
\end{bmatrix} \begin{bmatrix}
m_\theta \\
m_\phi
\end{bmatrix}
\]  

(II-52)

In the limit where the surface torque energy is much greater than the exchange energy, \( m_\theta, m_\phi = 0 \) and the surface spins are completely pinned. In the opposite extreme, \( \partial m_\theta/\partial y, \partial m_\phi/\partial y = 0 \) and the pinning condition is "natural." If both \( E_{\theta \theta}^s \) and \( E_{\phi \phi}^s \) are negative, \( \partial m/\partial y \) increases towards the surface and the surface spins are "unpinned." In this situation, a surface mode with imaginary wave-vector \( k_1 \) exists.

The solutions to Eq. (II-52) are the solutions Eq. (II-31), expressed here in an alternate form:
\[ m_\theta = \left[ G_1 \cos(k_1 y + \delta_1) + \gamma_1 e^{k_2 y} \right] e^{i\omega t}, \quad (\text{II-53a}) \]
\[ m_\phi = \left[ G_2 \cos(k_1 y + \delta_2) + \gamma_2 e^{k_2 y} \right] e^{i\omega t}. \quad (\text{II-53b}) \]

Here, \( G = (\alpha^2 + \beta^2)^{1/2} \) and \( \tan \delta = -\alpha/\beta \). Then in order to satisfy the boundary conditions (Stakelon, 1978)

\[ k_1 \tan \delta = \frac{k_2 \kappa_+ + \zeta \theta \zeta \phi}{k_2 + \kappa_-} \quad (\text{II-54}) \]

where

\[ \zeta^s = E^s / 2 G , \]
\[ \kappa_\pm = 1/2 \left( \zeta \theta \phi (1 \mp \sigma) + \zeta \phi \phi (1 \mp \sigma) \right) , \]
\[ \sigma = (1 - \Omega^+ \Omega^-)^{-1/2} , \]
\[ \Omega^\pm = \frac{i\omega/\gamma \pm \zeta \theta \phi \mu_0}{(E \theta \theta - E \phi \phi)/2\mu_0} \]

In this notation, the angle \( \delta \) is the spin wave phase shift at the boundary, while \( \sigma \) is a measure of the ellipticity of the precession. Also note that in satisfying the boundary conditions, the modes \( k_1 \) and \( k_2 \) are coupled.

6. Non-parallel Ground State

The surface anisotropy introduced to account for the physical boundary conditions in a thin film will, in general, result in a ground state in which the surface magnetization is at an angle compared to the bulk magnetization (Rado and Weertman, 1959), the so-called non-parallel ground state. The modifications to the theory can be found by letting the unit vectors, \( m_\theta \) and \( m_\phi \) in Eq. (II-25) become functions of \( y \), so that now

\[ \hat{M}(y,t) = M_0 \hat{\theta}(y) + m_\theta(y,t) \hat{\theta}(y) + m_\phi(y,t) \hat{\phi}(y). \quad (\text{II-55}) \]
The static response is found by balancing the surface torques arising from the anisotropy field and the exchange field.

\[ \tau_s = \frac{E_s^\theta}{\sin \theta} \hat{\theta} - E_s^\phi \hat{\phi} \]

\[ = \frac{2G}{M_o} \hat{\mathbf{M}} \times M_o \frac{\partial \hat{\phi}}{\partial y} \]

\[ = 2G \left( \theta' \hat{\phi} - \sin \theta \phi' \hat{\theta} \right) \tag{II-56} \]

Here \( \theta_o \) is the bulk equilibrium value \((\pi/2)\) and a prime denotes differentiation with respect to \( y \). This relation yields two boundary conditions

\[ \phi' = -\frac{E_s^\phi}{2G} \tag{II-57a} \]

\[ \theta' = -\frac{E_s^\theta}{2G} \tag{II-57b} \]

which, with Eq. (II-52), completely describe the surface.

The response of the bulk spins in the non-parallel ground state can be found by noting that in Eq. (II-26)

\[ \nabla^2 \mathbf{M} = M_o \frac{\partial^2 \mathbf{M}}{\partial y^2} \tag{II-58} \]

The bulk conditions are

\[ \theta'' - \sin \theta \cos \theta (\phi')^2 = \frac{E_\theta}{2G} \equiv \epsilon_\theta \tag{II-59a} \]

\[ \phi'' + 2 \cot \theta \theta' \phi' = \frac{E_\phi}{2G} \equiv \epsilon_\phi \tag{II-59b} \]

In order to evaluate the ground state configuration, the solution is linearized

\[ \theta(y) = \theta_o + \delta \theta(y), \tag{II-60a} \]

\[ \phi(y) = \phi_o + \delta \phi(y), \tag{II-60b} \]

and the form of the energy density \( E_s^S \) is substituted. As mentioned
previously, the surface anisotropy energy density is assumed to have uniaxial symmetry. In the usual geometry with \( \theta_0 = \pi/2 \), the energy derivatives are

\[
\begin{align*}
E^s_{\theta\theta} & = -2K^s \sin^2 \phi, \quad \text{(II-61a)} \\
E^s_{\phi\phi} & = -2K^s (\sin^2 \phi - \cos^2 \phi), \quad \text{(II-61b)} \\
E^s_{\theta\phi} & = 0. \quad \text{(II-61c)}
\end{align*}
\]

By substituting Eq. (II-60) and Eq. (II-61) into Eq. (II-59) and using the conditions of Eq. (II-57), the static configuration is found to be

\[
\begin{align*}
\delta \theta & = 0, \quad \text{(II-62a)} \\
\delta \phi & = \frac{1}{\Lambda} \frac{E^s_{\phi\phi}}{2G} e^{\Lambda y}, \quad \text{(II-62b)}
\end{align*}
\]

where

\[
\Lambda = (E^s_{\phi\phi}/2G)^{1/2}. \quad \text{(II-62c)}
\]

The effect of the surface anisotropy is to produce a canting of the surface spins with respect to the bulk spins. This canting produces in turn an additional torque on the magnetization which is felt in a region of a few decay lengths, \( \Lambda^{-1} \), from the surface. This additional torque must be taken into account when solving for the dynamic response of the system. The form of the bulk spin-wave modes will include an additional phase shift, \( \delta' \), due to this canting, so that

\[
m_0 \sim \cos (k_l + \delta + \delta').
\]

The equation of motion, Eq. (II-30) will be modified by the presence of the canted surface spins, since \( \delta \vec{E}^S \) from Eq. (II-49) has the form
The exchange torque of Eq. (11-51) now becomes

\[ \delta \tau^S = - \gamma \frac{M}{M_0} x \vec{V}E^S - \gamma \frac{M}{M_0} x \delta \vec{V}E^S, \]

\[ \delta \vec{V}E^S = \delta E^S \hat{\theta} + E^S \delta \hat{\theta} + \delta E^S \csc \theta \hat{\phi} + E^S \delta (\csc \theta) \hat{\phi} + E^S \csc \theta \delta \hat{\phi}. \]  

The exchange torque of Eq. (II-51) now becomes

\[ \delta \tau^S = \frac{2G}{M_0} \left\{ (\phi' \sin \theta m_{\theta} - \theta' m_{\theta}) \hat{r} - (\phi' \cos \phi m_{\phi} + m'_{\phi}) \hat{\theta} + (-\phi' \cos \phi m_{\phi} + m'_{\phi}) \hat{\phi} \right\}. \]  

Substituting the usual energy derivatives, the equation of motion is

\[ \frac{1}{\gamma} \frac{d m_{\theta}}{dt} = \frac{E_{\phi \phi}}{M_0} m_{\phi} - \frac{2G}{M_0} m''_{\theta}, \]  

\[ \frac{1}{\gamma} \frac{d m_{\phi}}{dt} = - \frac{E_{\phi \phi}}{M_0} m_{\phi} + \frac{2G}{M_0} \left\{ (\phi')^2 m_{\theta} + m''_{\theta} \right\}. \]  

The new boundary conditions are found by evaluating the effect of the spin canting on the transverse magnetization. To first order in \( \delta \phi \) and \( \delta \phi' \), these additional torques are

\[ \Delta \tau_\theta = \frac{E_{\phi \phi}}{M_0} \delta \phi m_{\phi}, \]  

\[ \Delta \tau_\phi = - \frac{E_{\phi \phi}}{M_0} \delta \phi m_{\theta} + \frac{2G}{M_0} (\delta \phi')^2 m_{\theta}. \]  

The first term in each equation gives the effect of the surface canting on the bulk torque, while the second term of Eq. (II-66b) is due to the additional exchange interaction between misaligned spins. Substituting the results of Eq. (II-62), the final form of the surface torques to first order is
The solution to the equation of motion is modified such that in Eq. (II-54) (Summers, 1978)

\[
\tau^s_\bar{\theta} = \frac{1}{M^s_0} \left[ E^s_{\theta\theta} - \frac{E^s_{\theta\phi}}{E^s_{\phi\phi}} E^s_{\phi} \right] m^s_\phi \quad \text{(II-68a)}
\]

\[
\tau^s_\phi = \frac{1}{M^s_0} \left[ -E^s_{\theta\phi} + \frac{E^s_{\theta\phi}}{E^s_{\phi\phi}} E^s_{\phi} + \frac{(E^s_{\phi})^2}{4G} \left( \frac{2G}{E^s_{\phi\phi}} \right)^{1/2} \right] m^s_\phi \quad \text{(II-68b)}
\]

Upon examining Eq. (II-54), it is found that the terms in $k^2$ will dominate and the boundary condition reduces to

\[
k^s_1 \tan \delta = K^s_+ \quad \text{(II-69)}
\]

In Figure 8, the dimensionless quantity $k^s_1 \tan \delta/(K^s_+/2\bar{G})$ is plotted as a function of $\zeta = \pi/2 - \phi$ for room temperature, experimental frequency 9.2GHz and the physical properties of the YIG film used in this experiment. Curve 1 corresponds to the parallel ground state approximation, curve 2 corresponds to the non-parallel ground state solution. The angle at which the curve crosses the abscissa is the critical angle at which only the uniform mode, $k^s_1 = 0$, is excited.

7. Critical Angle

The analysis presented in this section is applicable to a film with a single surface. Solutions to the problem of a thin film with two surfaces and symmetric boundary conditions may be found by reflecting a solution across the film's center layer, provided the
Figure 8. The angle dependence of the surface parameter for a uniaxial surface anisotropy and a bulk anisotropy as described in Section C-3. Curve 1 is for the case of a parallel ground state and curve 2 is for the case of a non-parallel ground state.
thickness of the film is much greater than $\Lambda^{-1}$. In general, however, the boundary conditions at the two surfaces are asymmetric. This problem has been solved only in the parallel ground state approximation (Banavar and Keffer, 1979).

A feature which is retained in the extension to two surfaces is the existence of the critical angle, as seen in Figure 8. This configuration corresponds to $k_1 = 0$. It is a linear mode which has the property of separating those angles (or boundary conditions) at which a surface mode exists from those at which only body modes are allowed. Figure 9 is a diagrammatic representation of the transverse magnetization across a film thickness for both symmetric and asymmetric boundary conditions. Here, the notation is due to Puszkarski with surface parameters $A$ and $B$ given as $A = 1 - a k_1 \tan \delta_A$, where $a$ is the lattice constant, and similarly for $B$ (Puszkarski, 1973). Note that the linear mode appears at different values of $A$ and $B$ for different mode numbers, or conversely that the boundary conditions are a function of mode number.

In the parallel ground state approximation (for which Figure 9 applies), the transverse magnetization will have the form

$$m_y = [\alpha \sin k_1 y + \beta \cos k_1 y] e^{-i\omega t}$$  \hspace{1cm} (II-70)

since the $k_2$ mode can be ignored. The form of the linear mode is found by letting (Banavar and Keffer, 1979)

$$k_1 \rightarrow 0 \text{ as } \alpha \rightarrow \frac{2\alpha}{ak_1} \text{ ; } y \in (-L, L)$$  \hspace{1cm} (II-71)

The spatial part of the result is
Figure 9. The first two spin wave modes for symmetric and nonsymmetric boundary conditions. The surface parameter $A$ refers to layer 0 and surface parameter $B$ refers to layer $L$. 
In the non-parallel ground state approximation, $k_2$ is included and the oscillation has the form

$$m_\theta(y) = \beta + \frac{2\alpha y}{a} + e^{k_2 y}$$  \hspace{1cm} (II-73)

The mode is linear across the film with extra amplitudes localized at the two surfaces. However, only the uniform or $\beta$ portion will couple to the rf field in a resonance experiment.

The dependence of the linear mode on the surface parameters has been given as (Puszkarski, 1972)

$$r = L (1-p),$$  \hspace{1cm} (II-74)

with $L$ the number of layers in the film,

$$r = \frac{AB-1}{AB+1} \text{ and } p = \frac{A+B}{AB+1},$$

for the parallel ground state and circular precession ($\alpha_2/\alpha_1 = 1$).

The spin precession in general is elliptical, with ellipticity

$$\left|\frac{\alpha_2}{\alpha_1}\right|^2 = \left|\frac{\beta_2}{\beta_1}\right|^2 = \frac{E\theta/\omega_{\phi} + Dk_2^2}{E\phi/\omega_{\phi} + Dk_1^2} \equiv |\epsilon|^2,$$  \hspace{1cm} (II-75a)

$$\left|\frac{\gamma_2}{\gamma_1}\right|^2 = \frac{E\theta/\omega_{\phi} - Dk_2^2}{E\phi/\omega_{\phi} - Dk_2^2} \equiv |\epsilon^{-1}|^2$$  \hspace{1cm} (II-75b)

where $D = 2\omega/M_\phi$. The relationship between $\epsilon$ and $\epsilon^{-1}$ can be seen by rearranging the dispersion relation with $\omega = 0$.

$$E\theta/\omega_{\phi} - Dk_2^2 = -(E\phi/\omega_{\phi} + Dk_1^2),$$  \hspace{1cm} (II-76a)

$$E\phi/\omega_{\phi} - Dk_2^2 = -(E\theta/\omega_{\phi} + Dk_1^2).$$  \hspace{1cm} (II-76b)

In the case $k_1 = 0$
The general boundary conditions for the linear mode is given by the secular equations:

\[ \begin{vmatrix} A-S_1 & A-e_2^q \\ -B+S_1 & B-e_2^q \end{vmatrix} = 0 \quad (\text{II-78a}) \]

for \( m_\theta \) and

\[ \begin{vmatrix} (A-C_1) & (A-e_2^q) \\ (B+C_1) & (B-e_2^q) \end{vmatrix} = 0 \quad (\text{II-78b}) \]

for \( m_\phi \). Here \( q_{1,2} = k_{1,2} a/2, C_1 = \cos q_1 (L+1)/\cos q_1 L + 1, \) and \( S_1 = \sin q_1 (L+1)/\sin q_1 L + L+1/L \).

*The full 4 x 4 determinant is given as equation (38) in Banavar and Keffer (1979) where they have generalized \( \gamma e^{k_2 y} \) as \( (\gamma \cos k_2 y + \delta \sin k_2 y) \). All cases they consider have \( \gamma = \delta \) and imaginary, which corresponds to the solution given here.
III MAGNETISM OF THE GARNETS

A. Crystal Structure

The iron garnet crystal system, first discovered by Bertaut and Forrat in 1956, has the general chemical formula \( \text{M}_3 \text{Fe}_5 \text{O}_{12} \), with \( \text{M} \) standing for a rare earth or yttrium ion (Bertaut and Forrat, 1956). The unit cell contains eight formula units and belongs to the space group \( O^{10}_{h} - \text{Ia 3d} \) (Wyckoff, 1953). The 96 oxygen anions form a cubic lattice with three types of interstices which are occupied by the metal cations. The smallest of these, the 24 "d" sites, have tetrahedral symmetry. The next larger sites, the "a" sites of which there are 16, have octahedral symmetry. The largest 24 sites, referred to as "c" or "dodecahedral" sites, are surrounded by eight oxygen ions defining a polyhedron with 12 faces and 18 edges. (The figure is not a regular dodecahedron.)

Figures 10 and 11 help clarify the complicated crystal structure. In yttrium iron garnet (YIG), ferric ions occupy the "a" and "d" sites, \( Y^{3+} \) ions occupy the "c" sites. The unit cell lattice constant for YIG is 1.2376 nm at standard temperature and pressure. Figure 10 shows the arrangement of cations in two octants of the unit cell (Pauthenet, 1958), while Figure 11 illustrates the oxygen coordination of the three sites (Gilleo and Geller, 1958). It can be seen by studying the two figures that any magnetic interactions between ferric
Figure 10. Array of cations in two octants of a garnet unit cell (after Pauthenet, 1958).

- Fe$^{3+}$ at "a" site
- Fe$^{3+}$ at "d" site
- Y$^{3+}$ at "c" site
Figure 11. The oxygen coordination of cations in YIG (after Gilleo, 1958).

© Fe$^{3+}$ at "a" site
● Fe$^{3+}$ at "d" site
○ Y$^{3+}$ at "c" site
ions occurs via an intervening oxygen anion, not by direct overlap of wavefunctions.

B. Superexchange

When a strong coupling occurs over longer distances than would be the case without intervening electrons, the interaction is said to be due to "indirect" exchange; in the case of insulators the indirect exchange mechanism is called "superexchange." The indirect couplings are not necessarily weak compared to direct couplings. For example, YIG has a Néel temperature of 550K, indicating a strong exchange interaction (Martin, 1967).

A simple model of the superexchange mechanism is shown in Figure 12 and Figure 13 for iron and oxygen ions. The ground state is the unperturbed, perfectly ionic state whose energy is independent of spin configuration since all oxygen electrons are spin paired and direct exchange between the iron ions is negligible. In the excited state, one electron is transferred from oxygen to one of the iron ions. Since $\text{Fe}^{3+}$ has five d-electrons, the added electron must become spin-paired with a d-electron. There are now two possible states for the system: a state of multiplicity 11 in which the remaining oxygen electron is parallel to the electrons in the unaffected iron ion, and a singlet state in which the oxygen electron is antiparallel to the iron electrons. The latter state is lower in energy (Martin, 1967) and so the total interaction is antiferromagnetic.
Figure 12. Schematic representation of a possible ground state in the superexchange of two Fe$^{3+}$ via O$^{2-}$.

Figure 13. Schematic representation of the two spin possibilities of an excited state in the superexchange process.
Alternatively, the true state of the system can be thought of as arising from a time average of the purely ionic state and the purely covalent state. The configuration represented as

\[ \uparrow\uparrow\uparrow\uparrow\uparrow \cdot \uparrow \cdot \downarrow\downarrow\downarrow\downarrow\downarrow \]

which is the lower energy, preferred configuration in the covalent state, persists in the ionic state as

\[ \uparrow\uparrow\uparrow\uparrow\uparrow \cdot \uparrow\uparrow \cdot \downarrow\downarrow\downarrow\downarrow\downarrow \]

resulting in an antiferromagnetic coupling between the iron ions.

The constructions discussed above are helpful in visualizing the process of superexchange, but numerical results based on these models are not at all satisfactory. Anderson has discussed the main difficulties (Anderson, 1963a) which are:

1. The exchange effects do not appear until the third order of perturbation theory; the non-magnetic terms are large and neither type of term appears to converge rapidly.

2. Other types of perturbations, for example, a transfer of two electrons, need to be included.

3. The need for overlap in the wavefunctions leads to difficulties, in particular nonorthogonality, in the choice of wavefunctions.

Anderson has suggested an alternative two-stage approach to the problem (Anderson, 1963b). In the first part of the problem, the spreading of iron d-orbitals by the crystal field of the oxygen lattice is computed. Then the direct exchange between the new longer-ranging orbitals is calculated, ignoring the intervening oxygen ions. The wavefunctions in this approximation are orthogonal; thus the
overlap integrals are zero and the values of the exchange integrals indicate ferromagnetic coupling. Anderson refers to this situation as "potential exchange." These Heitler-London wavefunctions are then perturbed with molecular orbital wavefunctions (configuration interaction). The additional hopping integrals lower the energy of the antiferromagnetically aligned state, but do not affect the energy of the spin aligned state. This effect is called "kinetic exchange." It is necessary to introduce experimentally-determined parameters to discover if the kinetic or potential exchange dominates in a particular system.

C. Ferrimagnetism

Harris has calculated the value of the iron exchange integrals in YIG from spin-wave resonance data and has found $J_{aa} = -6.35 \text{ cm}^{-1}$, $J_{ad} = -31.8 \text{ cm}^{-1}$ and $2J_{aa} \leq J_{dd} \leq J_{aa}$ (Harris, 1963). An iron ion tries to align antiferromagnetically with all its neighbors. Since $J_{ad}$ is at least twice as strong an interaction than $J_{aa}$ or $J_{dd}$, that interaction dominates. The result is a structure in which the three spins on the "d" sublattice are parallel, the two spins on the "a" sublattice are parallel, and the spins on the two sublattices are antiparallel to each other. Such a material is called a ferrimagnet.*

There exist detailed molecular field (Néel, 1948) and spin wave theories (Keffer, 1966) for general ferrimagnets. Each of the three

*If the number of spins on each sublattice is equal, the material is an antiferromagnet.
sublattices in a garnet may contain a different magnetic ion; for example, \((\text{YSmLu})_3 \text{(FeGa)}_5 \text{O}_{12}\) (AFAL, 1976) is a typical composition of a material used for industrial application. The interactions between magnetic sublattices results in a feature unique to ferrimagnetic materials, the compensation point. In fact, there are two compensation points; one at which the total magnetization \(M\) goes to zero, the other at which the total angular momentum \(\mathcal{J}\) goes to zero. In practice, these are usually close together. The existence of a compensation point is followed experimentally by measuring the magnetization of the material as a function of the relative amounts of magnetic ions, or as a function of temperature.

In a ferrimagnetic resonance experiment, the gyromagnetic ratio is replaced by an effective ratio

\[
\gamma_{\text{eff}} \equiv \frac{M}{\mathcal{J}} = \frac{M_A - M_B}{\mathcal{J}} \frac{1}{\gamma_A - \gamma_B}
\tag{III-1}
\]

for a two sublattice material. Near a compensation point for \(\mathcal{J}\), \(\gamma_{\text{eff}}\) becomes very large and changes sign (Wangsness, 1953).

The compensation behavior is illustrated in Figure 14 through Figure 19. Figure 14 shows the sublattice magnetization in gadolinium iron garnet (Gd IG) (Pauthenet, 1958). The magnetizations of the iron sublattices approximate a Brillouin function, but the magnetization of the rare-earth sublattice is very much distorted from that ideal. Figure 15 illustrates the total magnetization of Gd IG,
showing the compensation point at 250 K (Pauthenet, 1958). Figure 16 demonstrates the appearance of the compensation point with increased Gd\(^{3+}\) substitution in Gd\(_x\) Y\(_{3-x}\) Fe\(_5\) O\(_{12}\) (von Aulock, 1965). The effective g-factor (proportional to \(\gamma_{\text{eff}}\)) as a function of temperature is shown in Figure 17 for GdIG (Rodrique, et al., 1960).

The consequence of the substitution of a non-magnetic ion into an iron site is shown for total magnetization as a function of temperature and substitution in Figure 18 (Krahn, 1978) and for the effective g-factor as a function of substitution in Figure 19 (Gerhardstein, 1977) for (Y\(_{3-x}\) Ca\(_x\)) Fe\(_2\) (Fe\(_{3-x}\) Ge\(_x\)) O\(_{12}\).

The compensation features are not seen in pure YIG, since Y\(^{3+}\) is non-magnetic and the same magnetic ion occupies the "a" and "d" sublattices. One consequence of the epitaxial growth conditions of YIG onto a gadolinium gallium garnet (GGG) substrate is the production of a diffusion region in which Gd\(^{3+}\) and Ga\(^{3+}\) have partially substituted for Y\(^{3+}\) and "d" site Fe\(^{3+}\) respectively. The magnetic behavior in this region parallels that of an inhomogeneously substituted rare-earth garnet, so the results found for other systems can be applied. The substrate region is discussed in detail in Chapter V.
Figure 14. The temperature dependence of the sublattice magnetizations in GdIG (after Pauthenet, 1958).
Figure 15. The temperature dependence of the total magnetization of GdIG (after Pauthenet, 1958).
Figure 16. The temperature dependence of the magnetization of $\text{Gd}_x \text{Y}_{3-x} \text{Fe}_5 \text{O}_{12}$ for six values of $x$ (after von Aulock, 1965).
Figure 17. The temperature dependence of the effective g-factor of GdIG (after Rodrigue, 1960).
Figure 18. The temperature dependence of the magnetization of $(Y_{3-X}Ca_X)Fe_2(Fe_{3-X}Ge_x)O_{12}$ for six values of $X$. Negative magnetization refers to $X$ greater than the compensation value (after Krahn, 1978).
Figure 19. The variation of the effective g-factor at room temperature with substitution in \((Y_{3-x}Ca_x)(Fe_{3-x}Ge_x)O_{12}\) (after Gerhardstein, 1977).
IV. PROPERTIES OF THE METALS

The three metals used as additional layers evaporated onto the YIG thin film were aluminum, a diamagnet, chromium, an antiferromagnet, and vanadium, a paramagnet. In this chapter, the properties of these metals pertinent to the experimental conditions will be discussed. These are as bulk or polycrystalline magnetic materials and as cation substitutions in the garnet lattice.

A. Metal Cation Substitution into YIG

The pattern of site preferences of cations into the garnet system was deduced by Geller (1960). The tetrahedral and octahedral sites admit only those ions which, given the crystal field of the site, assume a spherical or pseudospherical electronic configuration. Within this limitation, the larger the ion, the greater the preference for the octahedral site. The largest ions present go into the "dodecahedral" site. The amount one ion is able to substitute for another is controlled by the relative sizes of all the cations involved, since the garnet structure is not easily distorted.

Trivalent aluminum, smaller than Fe$^{3+}$, enters the tetrahedral sites first. Pure Y$_3$Al$_5$O$_{12}$ is known and is soluble in all proportions with YIG. The effect of Al$^{3+}$ substitution is to reduce the saturation magnetization and Curie temperature (Harrison and Hodges, 1961). In contrast to the rare-earth metals, the metal ions of Group
III A have the effect of slightly decreasing the spin-wave resonance linewidth (Saunders and Green, 1961).

The only trivalent transition metal ions that enter the garnet structure are Sc\(^{3+}\), Cr\(^{3+}\) and Fe\(^{3+}\). The electronic requirement of substitution limits Cr\(^{3+}\) to the octahedral site, even though it is smaller than Fe\(^{3+}\) (Geller, 1960). This situation restricts the amount of Cr\(^{3+}\) which can enter the garnet to \(x \sim 0.3\) in \(Y_3Cr_xFe_{5-x}O_{12}\). The presence of Cr\(^{3+}\) increases the magnetization and the resonance linewidth relative to YIG (Saunders and Green, 1961).

Vanadium substitutes into the garnet structure as V\(^{5+}\), presumably entering only the tetrahedral sites (Geller, 1960). No studies have been made on any V-substituted garnet system.

B. Magnetic Structure of Cr

The magnetic nature of antiferromagnetic materials was not systematically studied until the advent of neutron diffraction. In a classic paper, Shull and Wilkinson investigated the magnetic structure of powdered samples of the transition metals (Shull and Wilkinson, 1953). They discovered that Cr was antiferromagnetic with a Néel temperature, \(T_N\), of 475K. The observed magnetic moment of 0.4\(\mu_B\) per atom was anomalously low compared to the atomistic prediction of 5\(\mu_B/\text{atom}\), a result which could not be accounted for by any existing theories.

Further neutron diffraction studies were carried out on single crystal Cr (Corliss et al., 1959). The picture which emerged was of
a body-centered cubic crystal with the body-centered spin antiparallel to the corner spin. The magnetic superstructure consisted of antiphase domains in which 180° spin reversals occurred about every 14 unit cells normal to the antiphase boundaries.

\[ +--+-+-+-+ +--+-+-+-+ +-- \text{ etc.} \]

Within a domain, the spins were parallel to the boundary; the boundaries were parallel to crystallographic faces. A macroscopic sample consisted of random regions in which the boundaries were parallel to a particular face.

The single crystal $T_N$ found by neutron diffraction is 312K, which agrees with the critical temperature associated with resistivity and lattice expansion, but not with the $T_N$ for polycrystalline samples. There is a third critical temperature in Cr, $T_S = 122K$ which is attributed to a spin-flip in which the spins become perpendicular to the antiphase domain wall (Bacon, 1961).

The antiphase domain model provided a convenient picture of the antiferromagnetic structure of Cr, but it could not account for all the facts. Overhauser proposed a new mechanism of antiferromagnetism based on the spin density wave (SDW) (Overhauser, 1959). An SDW is the sum of two change density waves (CDW) with axes of Quantization $\hat{e}$, one with spins parallel to $\hat{e}$, the other with spins antiparallel to $\hat{e}$. The CDW's have equal magnitude, but opposite phase. The wavevector $\hat{Q}$ of the SDW is determined by the exchange energy and wavelength of the electrons at the Fermi surface and so in general is incommensurate
with reciprocal lattice vectors. The SDW model can account for the higher Néel temperature found in powdered samples of Cr. The localized spins are oriented through their interaction with a static SDW in the conduction electron gas. Those spins lying near nodes of the wave will contribute little to the magnetic interaction energy. The mechanical imperfections found in powdered samples serve as nucleating sites where a domain can terminate if the wave nodes fall near lattice sites. A new domain with a more favorable correlation between the SDW phase and the lattice sites can begin. The net result is more spins near the maxima of the SDW's, a larger interaction energy and a higher Néel temperature (Griessen, et al., 1977).

The magnetic state of any given sample of Cr depends on its metallurgic and magnetic history. In a powdered sample or a single crystal which has been strained, magnetic order begins at a temperature between 312K and 480K. The larger the dislocation density, the higher the transition temperature. This state, AF₀, is a commensurate SDW state.

Below T_N = 312K, Cr has an incommensurate SDW state. The wave-vector of the SDW is \( \vec{Q} = \left( \frac{2\pi}{c} \right) (0,0,1±\delta) \) with \( \delta = 0.0496 \), measured by deHaas-van Alphen frequencies (Greissen, et al., 1977). It is uncertain whether the SDW's which exist in a "natural" sample are helical or linear, but application of a magnetic field while cooling through T_N can force a sample to have a single-\( \vec{Q} \) linear SDW (Arrott, 1966). The state below T_N, AF₁, is a transverse SDW state. When a magnetic field \( \vec{H}_0 \) is applied along a Cr <100> axis during cooling, \( \vec{Q} \) aligns
parallel to $\mathbf{H}_0$ with $\mathbf{M}$ perpendicular to $\mathbf{Q}$. Below the spin-flip transition at $T_s = 122K$, the state $\text{AF}_2$, a longitudinal SDW state with $\mathbf{M}$ parallel to $\mathbf{Q}$, exists. When the cubic crystal lattice distorts due to magnetostriction, $\mathbf{Q}$ prefers to align along the longest axis in the $\text{AF}_1$ state and along the shortest axis in the $\text{AF}_2$ state (Steinitz, et al., 1969). The spin-flip transition is first-order (Street, et al., 1968), but the sharpness of the transition depends on the strains in the sample. Figures 20 and 21 show magnetic phase diagrams for single crystal and powdered samples of Cr (Bacon and Cowlam, 1969).

C. Band Structures

1. Chromium

The existence of the spin-density-wave state in Cr has been connected with unique features in the structure of its electronic Fermi surface (Lomer, 1962, 1964). The Fermi surface is usually represented by its intersection with the first Brillouin zone, which is shown for body-centered cubic, paramagnetic Cr in Figure 22. Point $H$ has symmetry $O_h$; point $P$ has symmetry $T_d$; point $N$ has symmetry $D_{2h}$. The important features of the Fermi surface of paramagnetic Cr are:

(i) The number of electrons equals the number of holes.

(ii) All branches of the Fermi surface are closed.

(iii) There are two main branches; an electron surface centered on $\Gamma$, the origin of reciprocal space, and a hole surface centered on $H$. 

Figure 20. Magnetic phase diagram for perfect, single crystal chromium (after Bacon and Cowlam, 1969).

Figure 21. Magnetic phase diagram for powdered chromium (after Bacon and Cowlam, 1969).
Figure 22. The First Brillouin zone for paramagnetic, body-centered cubic chromium.
(iv) Smaller pockets exist, with holes centered on N, and electrons located on the [100] axes.

The intersection of the Fermi surface with 1/48 Brillouin zone faces is shown in Figure 23 (Asano and Yamashita, 1967). The electron surface around \( \Gamma \) and the hole surface around \( H \) have similar size and shape, but the hole surface is slightly larger.

If the magnetic transition in Cr resulted in a perfect antiferromagnet, the magnetic symmetry of the crystal would be reduced from a body-centered cubic to a CsCl-type structure. This state has been used as an approximation to the antiferromagnetic state of Cr, with the results shown in Figure 24. Due to the reduced symmetry, point \( H \) has been mapped onto point \( \Gamma \). The original electron and hole surfaces have coalesced, leaving the small surface on the axis.

In fact, the perfect antiferromagnetic state is not the ground state of Cr. The spin-density-wave state arises from an attempt to more perfectly nest the electron and hole surfaces, as shown schematically in Figure 25. The shift calculated by Asano is 0.05 \((2\pi/c)\), which agrees with experiment (Asano and Yamashita, 1967). To obtain quantitative agreement with the experimental value of the magnetic moment, it is necessary to introduce the next-nearest-neighbor interaction into the interatomic magnetic potential (Teraoka and Kanamori, 1977). The SDW lowers the energy of the system relative to a perfect antiferromagnetic state since it allows the antiferromagnetic interaction energy between next-nearest neighbors, which is less than but of the same order of magnitude as the nearest
Figure 23. The intersection of the Fermi surface with 1/48 Brillouin zone face for paramagnetic chromium (after Asano and Yamashita, 1967).
Figure 24. The intersection of the Fermi surface with 1/48 Brillouin zone face for antiferromagnetic chromium (after Asano and Yamashita, 1967).
Figure 25. The nesting of the hole surface about H in the electron surface about Γ, with the hole surface shifted by $\pm 0.04(2\pi/c)$ (after Lomer, 1962).
neighbor interaction energy, to contribute.

2. Vanadium

The problem presented by V is the absence of magnetic ordering in the bulk (Shull and Wilkinson, 1953), whereas the isolated atom has a magnetic moment of $3\mu_B$. There must then be some value of the lattice parameter for a hypothetical V crystal at which magnetic ordering begins.

One condition for the existence of a stable magnetic state is a high density of states at the Fermi surface (Slater, 1936). The energy levels of s- and d-electrons in V as a function of lattice parameter is shown in Figure 26 (Hatton, et al, 1973). The narrowing of the bands resulting in a high density of states at the Fermi surface is clearly seen. Magnetic ordering occurs at a lattice parameter of $a/a_0 = 1.18$, with $a_0$ the bulk equilibrium lattice parameter. This value is in good agreement with the V-V distance in gold- and aluminum-V alloys which have a magnetic moment.

D. Surface Magnetization

The possibility of a surface magnetic state which differs from the bulk state has been investigated by several authors (Mills, 1971, 1973; Desjonquères and Cyrot-Lackmann, 1976; Griffin, 1978). In the simplest calculation, molecular field theory is applied to a simple cubic lattice with a (100) surface and nearest-neighbor interactions (Weiner, 1973). For a temperature $T$ slightly greater than $T_C$, the cubic approximation to the Brillouin function for spin $S$ suffices,
Figure 26. Energy levels in vanadium as a function of lattice parameter. Magnetization begins just below 7.0 a.u. (after Hattox, et al., 1973).
and the molecular field equations are
\[ \eta(1) = \frac{\left[ h + \left( 4J_s / J \right) \eta(1) + \eta(2) \right] / 6 }{\tau} \]
\[ -\beta \left[ h + \left( 4J_s / J \right) \eta(1) + \eta(2) \right] / 6 \] \( / \tau^3 \)
\[ \eta(l) = \frac{\left[ h + \left( \eta(l+1) + 4\eta(l) + \eta(l-1) \right) / 6 \right] / \tau}{\tau^3} \]
\[ -\beta \left[ h + \left( \eta(l+1) + 4\eta(l) + \eta(l-1) \right) / 6 \right] / \tau^3, \]
\[ l \geq 2. \]

Here \( \eta(l) = \langle S_z(l)/S \rangle \) is a measure of the magnetization,
\( h = (S+1)g\mu_B H / 3k_B T \) is an applied field term, \( \tau = T/T_C \),
\( \beta = 3/5 \left[ S(S+1) + 1/2 \right] / (S+1)^2 \), \( J_s \) and \( J \) are the exchange integrals
for the surface and bulk layers, and \( l \) labels the crystal planes
parallel to the surface with \( l = 1 \) the surface layer. The linear
solution for a semi-infinite crystal in zero field is
\[ \eta(l) = \eta(l-1)/d, \]
\[ d = 1 + (6\epsilon + 9\epsilon^2)^{1/2} + 3\epsilon \]
where \( \epsilon \) is the reduced temperature \((T-T_C) / T_C \). Since \( d > 1 \), the
spontaneous magnetization decays exponentially away from the surface.
Substituting Eq. (IV-3) with \( l = 2 \) into Eq. (IV-1) yields the surface
spontaneous magnetization,
\[ \eta(1) = C\eta(1) - \beta C^3 \eta^3(1), \]
\[ C = \left[ 4(J_s / J) + 1/d \right] / [6(1+\epsilon)]. \]
For \( C > 1 \) and \( J_s / J > 5/4 \), there is a non-zero solution,
\[ \eta(1) = \left( (C-1)/8C^3 \right)^{1/2}, \]
as well as an \( \eta(1) = 0 \) solution. The non-zero solution is the
thermodynamically stable one.
Molecular field theory then predicts a spontaneous magnetization in the surface layer at a temperature above the bulk ordering temperature. The criterion $J_g/J > 5/4$ suggests that the phenomenon has its origin in the reduced symmetry of the surface. The decrease in the number of nearest neighbors at the surface leads to d-band narrowing (Weiner, 1973). If the increase in the density of states caused by the narrowing occurs near the Fermi level, magnetic order will result. The argument is also valid for the atoms next to chemical or mechanical defects.

Cr, with an atomic configuration of $(3d)^5 (4s)^1$, is an obvious candidate for surface magnetic order. It has been suggested that the commensurate antiferromagnetic state in stressed or powdered samples of Cr is an example of defect-induced magnetism (Teraoka and Kanamori, 1978). A decrease in the number of neighboring atoms has the same effect as an increase in lattice parameter, i.e., a narrowing of the d-bands (Fletcher, 1977; Hattox, et al., 1973).

A ferromagnetic surface state in Cr has been found experimentally (Ferguson, 1978). The method used was the detection of surface magnetoplasma waves by attenuated total reflection. The technique essentially measures the net magnetic moment of the surface. The Cr sample consisted of a 150 nm film evaporated onto a 90 nm film of MgF$_2$. Such a sample should continue to exhibit magnetic order above $T_N = 312K$, which was found to be the case.

The magnetic susceptibility of V fine particles (9-30 nm) has been measured (Akoh and Tasaki, 1978). The susceptibility was found
to obey the Curie-Weiss law with the Curie constant inversely proportionally to the radius of the sample suggesting that the moment originates at the surface. The magnetic transition temperature for the surface atoms was estimated at 2-3K.
V. EXPERIMENTAL PROCEDURE

A. Sample Preparation

The sample used in this experiment was a one-inch diameter disc of yttrium iron garnet grown on a gadolinium gallium garnet substrate. The method of growth employed was that of liquid phase epitaxy (LPE) (Linares, 1968; Shick, et al., 1971) using a horizontal dipping furnace (Blank, et al., 1973) located in this laboratory.

The thickness of the YIG film was measured using interference techniques (Pierce and Venard, 1974). A Cary 14 spectrometer was used to transmit electromagnetic radiation normal to the film. As the wavelength is swept from 2000 nm to 600 nm, conditions for destructive and constructive interference alternate, resulting in a transmission spectrum consisting of a series of interference maxima and minima. The index of refraction of YIG as a function of wavelength is known (Scott, et al., 1974) so the thickness can be calculated from the position of the extrema. The characteristics of the YIG sample are given in Table 1.

About 40 smaller samples were prepared from the large disc by cutting it along crystal axes into rectangles with a diamond-impregnated wire saw and then applying a small circular mask of Silicone RTV rubber adhesive to the surface (Stakelon and Gerhardstein, 1976). After the rubber cured, the unwanted garnet film was removed from around
Table 1. Characteristics of \( \text{Y}_2\text{Fe}_5\text{O}_{12} \) sample ADD-9 at room temperature.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>(0.56 \pm 0.02 \mu m)</td>
</tr>
<tr>
<td>(4\pi M)</td>
<td>1600 G</td>
</tr>
<tr>
<td>(g)</td>
<td>1.99</td>
</tr>
<tr>
<td>(D)</td>
<td>(5.92 \times 10^{-9} \text{ Oe cm}^2)</td>
</tr>
</tbody>
</table>

Table 2. Properties of the Metals.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cr</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>source</td>
<td>commercial foil</td>
<td>electroplated rod</td>
<td>.025 mm foil</td>
</tr>
<tr>
<td>purity</td>
<td>99.9%</td>
<td>99.99%</td>
<td>99.9%</td>
</tr>
<tr>
<td>melting point (°C)</td>
<td>660</td>
<td>1875</td>
<td>1900</td>
</tr>
<tr>
<td>atomic radius (Å)</td>
<td>1.18</td>
<td>1.18</td>
<td>1.22</td>
</tr>
<tr>
<td>Ionic* radius (Å)</td>
<td>0.51</td>
<td>0.63</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*For trivalent ion.
the mask and the backside of the substrate by etching in concentrated phosphoric acid at 100°C. The RTV mask was removed by softening it in a 2:1 mixture of dichloromethane and Beck Chemicals' T54 Epoxy Etch. The samples were finally cleaned by etching in the 100°C phosphoric acid for 30 seconds, followed by distilled water, acetone and Freon TF rinses. The disc-shaped samples were about 1 mm diameter.

The metals were evaporated onto the YIG samples in a bell-jar evaporator at 10^{-6} torr. Before evaporation of the metal, the garnet films were cleaned of any residual organic material by exposing them to ultraviolet light in a partial pressure of oxygen of 10^{-4} torr for four hours (Sowell, et al., 1976). This method is equivalent to cleaning by rf back-sputtering. The metal films were then evaporated to a thickness of 50 to 100 nm. Their properties are listed in Table 2.

B. Spectrometer

The microwave spectrometer used was a standard reflection cavity, balanced-bridge type (Poole, 1967; Alger, 1968). A schematic of the system is shown in Figure 27.

The microwave power at approximately 9.2 GHz (X-band) or 23.2 GHz (K-band) is generated by a reflex klystron. The microwaves pass through a ferrite isolator and variable attenuator to one part of a circulator. The isolator prevents the waveguide network from acting back and influencing the frequency stability of the klystron. The attenuator is necessary to control the level of power reaching the sample. The three-port circulator directs the microwaves into the resonant cavity.
Figure 27. Block diagram of the microwave resonance spectrometer.
The cavities used normally operates in the TE 101 or TE 102 mode, with the sample placed on the narrow-wall, garnet crystal axes aligned to the wall, at a point half-way up (TE 101) or a quarter of the way up (TE 102) the cavity wall. This positioning assures that the sample is at the maximum of microwave magnetic field intensity and that the microwave magnetic field is parallel to the plane of the film. It also minimizes dielectric losses by placing the sample at a minimum of microwave electric field intensity. Figure 28 illustrates the modes and the position of the sample in the cavity.

When the klystron is tuned to the cavity frequency and the cavity iris is adjusted, the waveguide is impedance matched (critically coupled) to the cavity. In this condition, no power is reflected up the waveguide to the circulator. In practice, this condition is not met and a small amount of power is reflected into the circulator. The circulator directs this reflected power through a wavemeter and into a crystal diode detector which gives a dc output proportional to the reflected power. This signal is fed into an automatic frequency control unit (AFC) which operates by phase detection. The AFC supplies a 10 KHz modulation to the reflector of the klystron. If the cavity is not resonant at the klystron frequency, the microwave power reflected from the cavity will be amplitude modulated at 10 KHz above and below the signal frequency. The dc potential proportional to the amplitude of the signal will thus be modulated by the 10 KHz signal. The AFC rectifies its output to the klystron with the correct polarity to reduce the frequency difference between the cavity and the klystron.
Figure 28. The microwave magnetic field and the sample in the resonant cavities.
At a resonant condition, microwave power is absorbed by the sample, causing a change in the Q of the cavity. The waveguide and the cavity are now impedance mismatched and power is reflected from the cavity to the circulator where it is fed to the crystal detector and into the display system. Sensitivity in the detection is significantly increased when ac methods are employed. To this effect, the magnetic field is modulated with a small audio frequency field. The source of the modulation signal is the reference oscillator in the lock-in amplifier. The signal is amplified and fed to a pair of Helmholtz coils mounted on the magnet pole faces. The usual modulation frequency was 400 Hz; the root mean square amplitude of the modulation field was 0.7 Oe.

The signal from the crystal diode is phase-detected by the lock-in amplifier. Since field modulation is used, the output to the Y-axis of an X-Y recorder is proportional to the first derivative of the absorption line. The X-axis of the recorder is controlled by the magnet sweep control which determines the range and speed of the sweep of the magnetic field.

The temperature of the sample was controlled by having the waveguide and cavity inside a Janis or Andonian variable temperature dewar. The temperature from 300 K to 4.2 K was monitored with a GaAs diode mounted on the microwave cavity and used in conjunction with a Princeton Applied Research Model 152 temperature controller. This arrangement could stabilize the temperature to within one degree. For temperatures below 15 K, a second temperature controller and diode mounted in the dewar's tail were used to preheat the He gas entering
the sample chamber. The temperature was maintained to within 0.3
degree.

To obtain temperatures below 4.2 K, the sample chamber was
flooded with liquid He and the pressure lowered by pumping. Pressure
stability was not consistently achieved until the pump valve was
opened fully and the temperature of the system was below the \( \lambda \)-point
of He (2.17 K). In order to monitor the liquid He level in the sample
chamber, two 1 K\( \Omega \) carbon resistors were used; one was placed near the
cavity, the other was placed half-way up the waveguide arm. The
resistance of these resistors was typically 30 K\( \Omega \) higher at any pres-
sure when the resistor was in liquid He than when it was in He gas.
The pressure in the system was monitored using a thermocouple guage
control. The lowest pressures attained were in the range of 1600 to
2300 mtorr, corresponding to about \( T = 1.4 \) K.
VI. SUBSTRATE SURFACE

In order to investigate any changes that are induced on the free surface of a thin garnet film, it is necessary to understand the contribution of the substrate surface to the data. In this chapter, previously reported facts about the condition of the YIG/GGG interface are analyzed to predict the behavior of the film used in this experiment.

The Puszkarski pinning parameters for a thin film can be analyzed in terms of Legendre polynomials, $P_i(\cos \phi)$.

$$A = 1 - \sum_i a_i P_i(\cos \phi),$$  \hspace{1cm} (VI-1)

and similarly for $B$. It has been found that, for YIG films, only the first two even-ordered terms are needed to completely describe the surface condition (Yen, et al., 1979). The isotropic term has a strong temperature dependence; all angle dependence appears in the uniaxial term which has only a slight temperature dependence.

During the growth of the magnetic film onto the substrate, a diffusion region of mixed composition occurs. The width and chemical composition of the diffusion region has been studied using Auger spectroscopy (Vittoria and Schelleng, 1977). It was found that the width of the diffusion region was independent of the film thickness for YIG films grown by liquid-phase epitaxy. The average diffusion width is 25 nm, about 5% of the thickness of a 0.56 μm film. The concentration of Gd$^{3+}$, Y$^{3+}$, Fe$^{3+}$ and Ga$^{3+}$ vary linearly across the
diffusion region. It is the effects of the changing interactions among the ions which leads to the substrate surface energy density.

A. Magnetization Profile

Vittoria and Schelleng attempted to model a potential energy profile across the diffusion region using their Auger data and molecular field theory (Vittoria and Schelling, 1977). However, they made the assumption that the molecular field coefficients were independent of composition, an assumption which is incorrect (Dionne, 1970). Summers attempted to correct this problem by using a model of ferrimagnetism based on site-to-site linkages (Gilleo, 1960) in his calculation of the energy profile across the substrate interface (Summers, 1978). However, he ignored the effects of linkage between "a"- and "d"-site iron ions and "c"-site rare-earth ions. Since it is this interaction between Gd\(^{3+}\) and Fe\(^{3+}\) which gives rise to the temperature-dependent isotropic term in the surface parameter, this calculation is not complete.

The calculation presented here attempts to incorporate the relevant body of empirical data on substituted garnets into the molecular field approach. The composition in the diffusion region is taken as

\[ Y_{3-X}Gd_XGa_YFe_{5-Y}O_{12}, \]

where \( X \) ranges from 0 to 3 and \( Y \) ranges from 0 to 5. Values of \( X \) and \( Y \) versus position in the diffusion region are taken from published data on an unannealed, LPE-grown YIG film (Vittoria and Schelleng, 1977).

The magnetization of a given sublattice is (see Chapter II)
\[ M_i(T) = M_i(0)B_i (S_i g_i u_i H_i / kT). \] (VI-2)

The magnetization at \( T = 0 \) is

\[ M_i(0) = 8N_i g_i u_i S_i / V \] (VI-3)

where \( V \) is the volume of the unit cell which contains 8 formula units. The volume is corrected for changing composition (Geiss, et al, 1971), but not for changing temperature. The \( N_i \) is the number per formula unit of magnetic ions corrected to reproduce experimental data.

\[ N_a = 2(1-y_a/2)(1-(y_d/3)^{5.4}), \quad (VI-4a) \]
\[ N_d = 3(1-.1y_a/2)(1-y_d/3), \quad (VI-4b) \]
\[ N_c = X. \quad (VI-4c) \]

Here, \( y_a \) and \( y_d \) are the amounts of \( \text{Ga}^{3+} \) in the octahedral and tetrahedral sites. The \( N_i \) can be thought of as the number of magnetic ions with enough nearest and next-nearest neighbors to be able to contribute to the net ferrimagnetism. This is the "linkage" theory.

Since \( \text{Ga}^{3+} \) prefers the tetrahedral site, \( y_a \) and \( y_d \) are determined by putting 90% of the substituting \( \text{Ga}^{3+} \) into the tetrahedral sites until they are filled (Czerlinsky, 1969):

- for \( 0 \leq Y \leq 3.33 \quad y_a = 0.1Y, \ y_d = 0.9Y; \)
- for \( 3.33 \leq Y \leq 5 \quad y_a = Y - 3, \ y_d = 3. \)

The approximations for \( N_i \) are very good for \( y_a \leq 0.70 \) and \( y_d \leq 1.95. \)
Beyond these points, canting of spin vectors within the sublattices occurs which decreases the magnitudes of the sublattice magnetizations at an increased rate. For values of \( y_a \) and \( y_d \) greater than the critical values, \( N_a \) and \( N_d \) are made to go quadratically to zero.

The values of the exchange fields, \( H_i \), are found by the equations

\[
H_i = \sum_j \lambda_{ij} M_j ,
\]  

(VI-5)

In terms of exchange constants, the molecular field coefficients are

\[
\lambda_{ij} = 2 \frac{z_{ij}}{N_j} \frac{\langle J_{ij} \rangle}{g^2 \mu_B^2} \frac{V}{8}
\]

(VI-6)

where \( z_{ij} \) is the number of "j"-site nearest neighbors of an "i"-site ion. The ratio \( z_{ij}/N_j \) remains constant with changing concentration, but \( \langle J_{ij} \rangle \) does not. Referring to Figure 29, it can be seen that if a "d"-site ion is replaced by a nonmagnetic ion, \( \langle J_{dd} \rangle \) remains unchanged, but the spin canting in the "a" sublattice results in a net decrease in the magnitude of \( \langle J_{aa} \rangle \) and \( \langle J_{ad} \rangle \). The molecular field coefficients are corrected empirically for composition*.

\[
\lambda_{aa} = -(4.895 \times 10^{24}) V (1 - 0.42 y_d).
\]

\[
\lambda_{dd} = -(2.289 \times 10^{24}) V (1 - 0.43 y_d).
\]

\[
\lambda_{ad} = -(7.305 \times 10^{24}) V (1 - 0.125 y_a) (1 - 0.127 y_d).
\]

\[
\lambda_{ac} = -(2.591 \times 10^{23}) V.
\]

\[
\lambda_{dc} = -(4.519 \times 10^{23}) V.
\]

\[
\lambda_{cc} = 0.00.
\]

(VI-7)

* The coefficients are those of Dionne (1971) converted to the units used here.
Figure 29. Schematic diagram showing how the loss of a magnetic ion in the "d" sublattice results in spin canting in the "a" sublattice and lowers the average value of $J_{aa}$ and $J_{ad}$. 
Again, these coefficients are good in the range \( y_a \leq 0.70, y_d \leq 1.95 \).

Beyond these points, the coefficients are made to go quadratically to zero.

For the magnetic ions considered, the \( J_i \) in the Brillouin function are the spin-only values; \( S = 5/2 \) for Fe\(^{3+}\) and \( S = 7/2 \) for Gd\(^{3+}\). Then for any value of \( X \) and \( Y \), Eq. (VI-2) and Eq. (VI-5) are solved self-consistently.

The results are shown in Figures 30 and 31. The roughness of the curves is a reflection of the scatter in the Auger data. From Figure 30 it is seen that the spontaneous magnetization of the "a" and "d" sublattices goes to zero as the amount of Fe\(^{3+}\) decreases. They reach zero together because the largest contribution to the exchange field felt by each Fe\(^{3+}\) sublattice is due to the magnetization of the other. The magnetization of the "c" sublattice at first increases as the Gd\(^{3+}\) concentration increases, then decreases due to decreasing Fe\(^{3+}\) concentration.

The total magnetizations for five temperatures are shown in Figure 31. They were calculated from

\[
M = M_a + M_d + M_c ,
\]

and show that the "c" sublattice orders antiferromagnetically with respect to the "d" sublattice. This is found to be true for Gd\(^{3+}\) as the substituting rare-earth ion and for the concentrations found in the part of the interface region where there is a finite magnetization (Brandle and Blank, 1976). Note that there is a compensation point in
Figure 30. The sublattice magnetizations across the diffusion region for $T = 300K$. 
Figure 31. The total magnetization across the diffusion region for $T = 300K$, $150K$, $50K$, $10K$ and $1.4K$. 
the total magnetization about one quarter of the distance into the diffusion region. The second compensation point for $T = 10K$ and $T = 1.4K$ reflects the fact that $\lambda_{ac}$ and $\lambda_{dc}$ were not corrected for decreasing Fe$^{3+}$ concentration.

B. Energy Profile

In order to evaluate the effect of the changing magnetization in the diffusion region on the equations of motion, it is necessary to carry out the analysis of Chapter II given that the saturation magnetization is a function of $y$:

$$\dot{M} = M_0(y) \hat{f} + m_\theta(y,t) \hat{\theta} + m_\phi(y,t) \hat{\phi}. \quad (VI-9)$$

The conditions at static equilibrium are unchanged, that is $E_\theta, E_\phi = 0$, but in the first-order dynamic case there is an additional component in $\delta t$. (Compare Eq. (II-28d).) Now

$$\delta (\dot{M} \times \nabla M) = [(m_\phi \nabla^2 M_0 - M_0 \nabla^2 m_\phi) \hat{\theta}$$

$$\quad - (m_\theta \nabla^2 M_0 - M_0 \nabla^2 m_\theta) \hat{\phi)]. \quad (VI-10)$$

The equations of motion are:

$$\frac{1}{Y} \frac{dm_\theta}{dt} = \frac{1}{M_0} \left( E_{\theta \phi} + \frac{2G}{M_0} \frac{d^2 M_0}{dy^2} - \frac{2G}{M_0} \frac{d^2}{dy^2} \right) m_\phi, \quad (VI-11a)$$

$$\frac{1}{Y} \frac{dm_\phi}{dt} = - \frac{1}{M_0} \left( E_{\theta \phi} + \frac{2G}{M_0} \frac{d^2 M_0}{dy^2} - \frac{2G}{M_0} \frac{d^2}{dy^2} \right) m_\theta, \quad (VI11b)$$

where the values of $E_{\theta \phi} = 0$ and $\theta = \pi/2$ have already been set. Substituting the general form of $m_\theta$ and $m_\phi$, Eq. (II-31), and, for
simplicity, neglecting the crystalline anisotropy energy and the term in \(k_2\), the equations become

\[
\frac{i\omega}{\gamma} m_\theta = [H \cos(\phi - \phi_H) + 4\pi M_o \cos2\phi + \frac{2G}{M_o} \frac{d^2M_o}{dy^2} + \frac{2G}{M_o} k_2]m_\phi, \quad (VI-12a)
\]

\[
-\frac{i\omega}{\gamma} m_\phi = [H \cos(\phi - \phi_H) - 4\pi M_o \sin^2\phi + \frac{2G}{M_o} \frac{d^2M_o}{dy^2} + \frac{2G}{M_o} k_2]m_\theta \quad (VI-12b)
\]

Transforming the angle \(\phi\) to the angle \(\zeta\) as in Chapter II, the dispersion relation becomes (compare Eq. (II-45))

\[
\left(\frac{\omega}{\gamma}\right)^2 = [H \cos(\zeta - \zeta_H) - 4\pi M_o \cos2\zeta + \frac{D}{M_o} \frac{d^2M_o}{dy^2} + Dk^2]
\]

\[
\times [H \cos(\zeta - \zeta_H) - 4\pi M_o \cos^2\zeta + \frac{D}{M_o} \frac{d^2M_o}{dy^2} + Dk^2], \quad (VI-13)
\]

where \(D\) is the dispersion constant.

For the case of an applied field perpendicular to the film plane, \(\zeta = \zeta_H = 0\) and the dispersion relation becomes

\[
\left(\frac{\omega}{\gamma}\right) = H - 4\pi M_o \frac{d^2M_o}{dy^2} + Dk^2. \quad (VI-14)
\]

It is then possible to select a linear combination of \(m_\theta\) and \(m_\phi\) which yields a Schröedinger equation for the transverse magnetization.

\[
D \frac{d^2m}{dy^2} \left[ \frac{\omega}{\gamma} - (H - 4\pi M_o \frac{d^2M_o}{dy^2}) \right]m = 0. \quad (VI-15)
\]
Here $D$ is analogous to $\hbar^2/2m$ and the potential, $V_1$, is given by the terms in parentheses.

For the case of an applied field parallel to the film plane, $\zeta = \zeta_H = \pi/2$, and the dispersion relation becomes

$$\left(\frac{\omega}{\gamma}\right)^2 = (H_\parallel + 4\pi M_o + \frac{D}{M_o} \frac{d^2M}{dy^2} + Dk^2)(H_\parallel + \frac{D}{M_o} \frac{d^2M}{dy^2} + Dk^2), \quad (VI-15)$$

from which it is not possible to derive a simple second-order differential equation. If $4\pi M_o$ is less than $H_\parallel$, Eq. (VI-15) can be reduced to

$$\left(\frac{\omega}{\gamma}\right)^2 = H_\parallel + 2\pi M_o + \frac{D}{M_o} \frac{d^2M}{dy^2} + Dk^2, \quad (VI-16)$$

which is good to within 5% for YIG at 9.2 GHz. The corresponding Schroedinger equation is

$$D \frac{d^2m}{dy^2} + \left[\frac{\omega}{\gamma} - (H_\parallel + 2\pi M_o + \frac{D}{M_o} \frac{d^2M}{dy^2})\right]m = 0, \quad (VI-17)$$

with $V_\parallel$ given by the terms in parantheses.

These two potentials are shown in Figure 32 for the two lowest temperatures and an assumed diffusion region width of 25 nm. To generate these curves, it was necessary to calculate $M_o$ at many more points than are present in the data; it was assumed that Gd$^{3+}$ and Ga$^{3+}$ diffuse an equal distance into YIG. Then the differentiations of $M_o$ were done numerically. It is seen that at very low temperatures, $V_\parallel$ displays a potential well. The dependence of the shape of this well on the assumed diffusion width is shown in Figure 33. The dashed
Figure 32. $V_{\parallel}$ and $V_{\perp}$ for $T = 10$K and 1.4K and a diffusion width of 25 nm.
Figure 33. $V''$ (normalized to $H'' + 2\pi M_s$) for $T = 1.4K$ and two diffusion widths. The dotted curve is the best fit Morse potential for $W = 50$ nm. The value of $\beta$ corresponds to a full-width-at-half-minimum value of 3.1 nm.
curve is a Morse potential approximation for a 50 nm diffusion width. The Morse potential has the form

\[ V = A(e^{-2\beta(y_e-y)} - 2e^{-\beta(y_e-y)}) \]  

(VI-18)

where A is the depth of the well, \( \beta \) is a measure of the width of the well, and \( y_e \) is the distance of the potential minimum. The energy of any state trapped in the well is given by (Landau and Lifshitz, 1958)

\[ -E_n = A[1 - \beta \sqrt{\frac{D}{A}} (n + 1/2)]^2 \]  

(VI-19)

where \( n \) is a non-negative integer. Therefore, for a bound state to exist, it must be that

\[ \frac{1}{\beta} \sqrt{\frac{A}{D}} > 1/2. \]  

(VI-20)

Reasonable values of the diffusion width are not large enough to produce a trapped mode.

C. Effective Anisotropy

The potentials due to changing magnetization can be converted to substrate "surface" anisotropy fields by deleting those terms which are common to the bulk and the interface. Thus,

\[ H_{\perp}^S = -4\pi(M - M_S) + D \frac{d^2M}{dy^2}, \]  

(VI-21a)

\[ H_{||}^S = 2\pi(M - M_S) + D \frac{d^2M}{dy^2}, \]  

(VI-21b)
where \( M_S \) is the bulk saturation magnetization. An effective surface
anisotropy constant is related to the field by \( H^S = 2K^S/M \). \( K^S \) has
both an isotropic and a uniaxial term:

\[
K^S = \frac{D}{2} \frac{d^2 M}{dy^2} - \pi M (M - M_S) (3 \cos^2 \zeta - 1).
\]

(VI-22)

It is seen from Figure 34 that all of the diffusion width dependence
and most of the temperature dependence are in the isotropic term.

A value for the uniaxial surface anisotropy constant can be
obtained from experimental data using Eq. (11-32) and Eq. (11-69) and
calculating the shift in the precession phase, as \( \tan \delta \), that the
potential in the diffusion region produces. A phase shift due to an
isotropic energy term cannot be found using the continuum model.
(Such a term does not contribute to the torque.) The effect of an
isotropic surface energy density has been calculated using a micro­
scopic model (Summers, 1978). The result is

\[
\tan \delta = \frac{(\alpha - 1 + I) \cos ka + 1}{\sin ka}
\]

(VI-23)

where

\[
I = \frac{\alpha}{\Delta - 1 + 2 \cos ka},
\]

\[
\Delta = \beta/\omega_e,
\]

\[
\beta = (\Delta \gamma) H,
\]

\[
\omega_e = \frac{\omega - \omega_0}{k^2 a^2}.
\]
Figure 34. The anisotropy constant across the diffusion region as a function of temperature and diffusion width.
$S_{\text{Gd}} = a S_{\text{max}},$ $k$ is the bulk spin wavenumber, $a$ is the bulk lattice parameter, $\Delta \gamma$ is the difference in the gyromagnetic ratios of Fe$^{3+}$ and Gd$^{3+}$, $H$ is the resonant field, $\omega$ is the experimental frequency, and $\omega_0 = \gamma H$, with $\gamma$ referring to Fe$^{3+}$.

D. Impurity Inclusions

The changing composition in the diffusion region is not the only source of anisotropy at the substrate interface. During the growth of the thin garnet film, lead from the flux and platinum from the crucible and tools are incorporated into the crystal structure. The amount of each is determined mainly by the growth temperature and amount of supercooling. For the conditions under which the film used in this experiment were grown, the amount of lead in the bulk is between 1.0 and 1.5 wt % (Robertson, et al., 1974). The amount of platinum is essentially constant and equal to about .02 atoms per formula unit (measured when it is equal to .5 wt % Pb) (Elliott, 1975).

The lead exists as Pb$^{2+}$, a large ion which can only enter the "c" site. The amount of distortion due to the Pb has been measured as between .02 and .05 nm/atom (Davies, et al., 1976). This distortion is large enough to allow Y$^{3+}$ to enter the "a" sites at the expense of Fe$^{3+}$. The amount of octahedrally-coordinated Y$^{3+}$ is only slightly less than the amount of Pb$^{2+}$.

Platinum also enters the "a" sites, as Pt$^{4+}$. The effect of Pt$^{4+}$ is to slightly decrease the lattice constant. Since the amounts
of \( \text{Pb}^{2+} \) and \( \text{Pt}^{4+} \) are generally not equal, there must be another source of charge compensation. Consequently, \( \text{Fe}^{3+} \) either reduces to \( \text{Fe}^{2+} \) which has a strong "a" site preference or oxidizes to \( \text{Fe}^{4+} \) (Glass and Elliott, 1974). An alternate method of charge compensation is the creation of an oxygen vacancy in the \( O^{2-} \) lattice.

Thus, there is both a growth-induced and a stress-induced anisotropy due to the presence of impurities. The strain caused by lattice misfit has been shown to be elastic (Brice, et al., 1975), resulting in a uniaxial anisotropy if the film is in tension or a biaxial anisotropy if the film is in compression. The complicated patterns of site preferences of the species \( \text{Pb}^{2+}, \text{Pt}^{4+}, \text{Y}^{3+} \) and \( \text{Fe}^{2+} \) results in a uniaxial anisotropy.

The impurity incorporation exists throughout the film, but the concentration profile is not constant across the width of the film. There exists a Pb-rich area next to the substrate about 0.1 \( \mu \text{m} \) wide (Davies, et al., 1976). There are two mechanisms responsible for the higher Pb concentration in this region, the condensation of PbO onto the substrate before it is immersed in the flux and the initial, transient growth kinetics of the garnet crystallization (Robertson, et al., 1974; Davies, et al., 1976). The region is clearly defined and its properties sufficiently different from those of the bulk that the anisotropies occurring there can be regarded as surface anisotropies. If the change in magnetization is slow compared to the changes in the diffusion region, the Pb-rich region may enlarge the width of the parallel potential well of Figure 33 without
affecting its depth. Then the existence of a bound state will depend on the depth of the well which is a function of temperature.
VII. RESULTS

A. Control YIG

The ferromagnetic resonance spectra of a control sample of LPE-grown, unannealed YIG was studied as a function of angle from 1.4 K to 400 K. A typical room temperature spectrum is shown in Figure 35. The modes shown correspond to \( n = 1, 3 \) and 4. The mode corresponding to \( n = 2 \) is buried in the magnetostatic modes immediately downfield of the \( n = 1 \) mode. The intensity of the highest-field mode is three orders of magnitude larger than the lower-field modes, which signifies a small surface anisotropy. Under these conditions, the surface anisotropy can be approximated by (Waksmann, et al., 1968)

\[
K^2 = \frac{n^2 \pi^2}{2L} \sqrt{\frac{I_n}{I_0}},
\]

(VII-1)

where \( L \) is the thickness of the film and \( \frac{I_n}{I_0} \) is the ratio of the intensities of the \( n \)-th order mode to the highest-field mode (which is approximately the \( n=0 \), uniform mode). For the spectrum shown, \( n=3,4 \) and \( |K^s| = 0.008 \pm 0.002 \text{ erg/cm}^2 \). The large uncertainty is due to the error in the measured intensity ratios; still \( |K^s| \) compares favorably with other published values (Vittoria and Schelleng, 1977) for an anisotropy located at the free surface.

A method to calculate the anisotropy at both surfaces is to solve the characteristic equation (Puszkarski, 1972)

\[
\tan k_1 L = \frac{r \sin k_1 a}{\cos k_1 a - p},
\]

(VII-2)

95
Figure 35. The perpendicular resonance spectrum of the control sample at 23.2 GHz and room temperature.
which is a generalization of Eq. (II-74). For given values of the
surface parameters \(A, B = 1 - ak_\perp \tan \delta_{A, B}, k_\perp\) is found from Eq. (VII-2)
and the field spacings between modes and the intensity ratios of modes
Corresponding to that \(k_\perp\) are compared with experimental results.
\(A\) and \(B\) are varied until the best fit to the data (measured by a
minimum \(\chi^2\)) is obtained. The values of \(K^S\) thus obtained are
\(K_A^S = 0.006 \pm 0.003\) and \(K_B^2 = 0.000 \pm 0.003\) erg/cm\(^2\) at perpendicular applied
field, and \(K_B^S = 0.009 \pm 0.003\) and \(K_A^S = -0.006 \pm 0.003\) erg/cm\(^2\) at parallel
field, where \(A\) refers to the free surface and \(B\) refers to the sub­
strate surface. Since there is a critical angle, the anisotropy con-
stant can be separated into isotropic and uniaxial parts. \(K^S(\text{iso}) =
-0.002 \pm 0.003\) and \(K^S(\text{uni}) = 0.008 \pm 0.003\) erg/cm\(^2\) at the free surface;
\(K^S(\text{iso}) = 0.006 \pm 0.003\) and \(K^S(\text{uni}) = -0.006 \pm 0.003\) erg/cm\(^2\) at the sub­
strate surface.

The material parameters can be calculated from the spectrum at
perpendicular resonance. According to Eq. (VI-14), only the resonant
applied field depends on the frequency of the experiment; the other
terms are dependent on material characteristics only. If the perpen­
dicular resonance is found at two frequencies, for example 9.2 GHz and
23.2 GHz, then the material constants can be eliminated and Eq. (VI-14)
solved for \(\gamma\) or \(g = \gamma h/\mu_B\).

Given \(\gamma\), Eq. (VI-14) can be used to find \(D\) and \(4\pi M\) by finding the
best-fit straight line of the resonant fields of the modes versus the
square of the mode number. Then the intercept is \((\omega/\gamma - 4\pi M)\) and the
slope is \((-D\pi^2/L^2\)). The results are \(D = 5.9 \times 10^{-9}\) Oe cm\(^2\) and
\[ 4\pi M = 1600 \text{ G}, \text{ giving a calculated value of } G = 3.8 \times 10^{-7} \text{ erg/cm. Typical values previously reported are } D = 5.2 \times 10^{-9} \text{ Oe cm}^2 \text{ and } G = 3.7 \times 10^{-7} \text{ erg/cm} \text{ (Gerhardstein, 1977). The value of } 4\pi M \text{ includes any bulk uniaxial anisotropy; the presence of Pb}^{2+} \text{ throughout the film also affects the magnetization. For these reasons, the value of } 4\pi M \text{ should not be compared unfavorably with the reported value for pure YIG of 1780 G (von Aulock, 1965).}

The results of the low temperature study of the control film are shown in Figures 36, 37, and 38. Figures 36 and 37 exhibit the typical linewidth maximum around 50 K due to rare earth impurities. The data in Figure 38 are more interesting, dividing the scale into two regions. From 300 K to 100 K, there are no changes in the film boundary conditions as reflected by the spacing of the first two modes. Below 100 K, the second mode in perpendicular resonance becomes more intense. Below 40 K, the highest-field mode becomes a surface mode and moves upfield rapidly as the temperature is decreased. As the surface mode becomes more localized, its intensity decreases. This behavior indicates that the surface anisotropy at one surface is changing rapidly.

The spectrum of the control film was also investigated below the \( \lambda \)-point of liquid He. The parallel resonance spectrum of 1.4 K is shown in Figure 39, and, although distorted, gives evidence of a surface mode. The analysis of Chapter VI indicates that this surface mode is localized at the substrate surface. The effect of the changing magnetization near the substrate as approximated by a Morse potential on the spin waves was investigated. The depth of the Morse potential well was determined by the temperature and a probable
Figure 36. The linewidth at parallel resonance as a function of temperature for the control sample.

Figure 37. The linewidth at perpendicular resonance as a function of temperature for the control sample.
Figure 38. The spacing between the first two modes as a function of temperature for the control sample.
parallel resonance
9.2 GHz
T=1.4K

Figure 39. The parallel resonance spectrum of the control sample at 9.2 GHz and T = 1.4K.
Ga\textsuperscript{3+}-Gd\textsuperscript{3+} diffusion width of 25 nm. The width of the potential well was expanded to 0.05 \(\mu\)m to include the effects of Pb\textsuperscript{2+}. The free surface was defined zero and the minimum of the potential was placed at the measured value of the film's thickness, 0.56 \(\mu\)m.

The results for the first three body modes and a bound surface mode are shown in Figure 40. The boundary condition at the free surface was taken as \(\frac{\partial}{\partial y} m = 0\). The body modes were found numerically using the Numerov method (Hamming, 1962). The form of the bound state is known analytically (Landau and Lifshitz, 1958) and is

\[
m(y) = e^{-\xi/2} \xi^s F(-n, 2s+1, \xi),
\]

where

\[
\xi = 2 \sqrt{\frac{A}{B}} e^{-\beta(y_e - y)},
\]

\[
2s+1 = 2 \sqrt{\frac{A}{B}} - 2n,
\]

and \(F(-n, 2s+1, \xi)\) is the hypergeometric function

\[
F(\alpha, \gamma, \delta) = 1 + \frac{\alpha \delta}{\gamma \Gamma} + \frac{\alpha(\alpha + 1) \delta^2}{\gamma(\gamma + 1) \Gamma} + \ldots.
\]

That function reduces to a polynomial since \(n\) is a non-negative integer. For the mode shown, \(n = 0\) and \(E = -52\) Oe, which roughly corresponds to the spacing of the surface mode and the first body mode shown in Figure 39. In Figure 40, it is seen that a potential which has a large enough well to trap a surface mode is strong enough to completely pin the body modes. The resulting phase shift relative to the uniform mode approaches \(\pi/2\) and according to Eq. (II-69), \(K^s\) at the substrate surface at low temperatures approaches infinity.
Figure 40. The first three body modes and a bound state (solid curves) in a film with a Morse potential (dotted curve) at the substrate surface. The potential parameters are $\Lambda = 170$ Oe, $\beta = 7 \times 10^5$ cm$^{-1}$ and $y_e = 5.6 \times 10^{-5}$ cm. The amplitudes of the modes are arbitrary.
B. Aluminum on YIG

The Al/YIG samples were prepared by evaporating Al to a thickness of 50 to 100 nm onto the YIG. The only effect of this treatment on the resonance spectrum was to increase the resonance linewidth to 1.2 Oe. The cause of this increase is an increase in surface imperfections due to the granularity of the Al (Wolfe and Johnson, 1975). The samples were then annealed at 550°C in a nitrogen atmosphere. The temperature chosen is below the melting point of Al and much lower than the growth temperature of YIG, assuring that no significant changes occur at the substrate surface. The nitrogen provided a non-oxidizing environment. Samples were annealed from 1/2 hr to 6 hr; the length of the anneal did not affect the results.

After the anneal, the appearance of the deposit changed from a shiny, metallic surface to a dull, gray, flaky one. This deposit was removed from the garnet by a 30 s etch in phosphoric acid at 65°C. After the total treatment, the garnet was visibly darkened, which is indicative of a high concentration of reduction-associated defects in the film (LeCraw, et al., 1975).

The parallel resonance spectrum for a sample annealed for one hour is shown in Figure 41. The highest-field mode is a surface mode associated with a region of decreased magnetic potential. The behavior of the linewidth of this mode and the spacing of the first three modes is shown in Figures 42 and 43. The peak in linewidth coincides with a critical temperature, T=180 K, indicated by the minimum in $I_2/I_1$ (and in $I_2/I_1$, which is not shown). Above this critical temperature, the
Figure 41. The parallel resonance spectrum at 9.2 GHz and T = 300K for an Al/YIG sample which was annealed for 1 hr at 550°C in a nitrogen atmosphere.
Figure 42. The linewidth at parallel resonance as a function of temperature for the Al/YIG (1 hr anneal) sample.

Figure 43. The spacing between the second mode and the first and third modes as a function of temperature for the Al/YIG (1 hr anneal) sample.
critical angle is constant; $\zeta_c = 49^\circ$. Below $T = 180$ K, the second mode reappears at the spacing which it maintains down to $T = 90$ K. The intensity ratio $I_2/I_1$ slowly increases as the temperature is decreased. In this region, $\zeta_c = 44^\circ$.

In order to discover where the surface mode was localized, the film was systematically etched in phosphoric acid at 85°C. The result of this process on the intensities and mode spacings is displayed in Figures 44 and 45. When the etching experiment was completed, the spectrum of the sample was essentially identical to that of the control sample, showing that the anisotropy which caused the surface mode was located at the free surface. The amount of material removed during the etch is not well known. One experimental etch rate for YIG in phosphoric acid (A.A. Parker, private communication) indicated that the thickness of garnet removed was more than the original measured thickness of the sample. The temperature dependence of this etch rate was used to correct the total time of etch for the small changes in the temperature of the solution which occurred during the experiment. An etch rate for YIG grown by chemical vapor deposition (Yen, 1977) suggests that 80% of the film was removed. Because of the Pb and Al impurities present in this sample, this estimate is thought to be high.

There are two mechanisms which could operate in this system. First, $\text{Al}^{3+}$ could diffuse into the garnet during the anneal and replace $\text{Fe}^{3+}$. Since $\text{Al}^{3+}$ prefers the tetrahedral site, this process would decrease the magnetization. It would also produce a strain-induced
Figure 44. The ratio of the room temperature intensities of the second mode to the first mode as a function of total time etched in phosphoric acid at 84°C for Al/YIG (1 hr anneal) sample.
Figure 45. The separation of the first two modes as a function of total time etched in phosphoric acid at 84°C for an Al/YIG (1 hr anneal) sample.
anisotropy in the diffusion region. Second, Al could reduce the garnet film, becoming \( \text{Al}_2\text{O}_3 \). Each oxygen vacancy produced in the garnet would have two \( \text{Fe}^{2+} \) ions associated with it. Since \( \text{Fe}^{2+} \) prefers the octahedral site, the net effect would be to increase the magnetization. In addition to the strain effects of missing \( \text{O}^{2-} \), there is a large magnetostriction due to the unquenched orbital angular momentum of \( \text{Fe}^{2+} \). The magnetostriction is expected to depend on temperature.

The results can be analyzed in terms of a region of altered magnetic potential at the free surface. Although the procedure of Chapter VI indicates the form this potential will take, it will be more convenient to consider the etch results if the potential is taken to be a square well or barrier. There is only one mode trapped in the potential well since there is only one critical angle. The question to be answered is whether the Al anneal treatment resulted in a potential well or a potential barrier at the film's free surface. In either case, the lowest energy mode (surface mode) will have no nodes and will be trigonometric in the well region and hyperbolic outside of it. The next mode will have one node and be trigonometric everywhere.

As the width of a well is decreased by etching, the energy of the trapped mode will increase much more rapidly than the energy of the trigonometric mode. Therefore, \( H_1 - H_2 \) will decrease. As the width of a barrier is decreased by etching, the energy of the trapped mode decreases, while the energy of the trigonometric mode increases rapidly. Therefore, \( H_1 - H_2 \) will increase. Figure 45 shows a slow decrease in the
mode spacing as the film is etched, verifying the former model. When
the potential well has been completely removed, the trapped mode
becomes the first trigonometric mode. As the thickness of the film is
further decreased, the energy of the modes increases approximately as
\( n^2/L^2 \); therefore, the mode spacing should start to increase. This
trend is evident in Figure 45.

A depth and width for the well were found using the facts that
\( I_2/I_1 = 0.5, H_1 - H_2 = 22 \text{ Oe} \), and that only one mode is trapped. The
energies of the allowed modes were found from the conditions (Schiff,
1968)

\[
k_1 \tanh k_1 t - k_2 \tanh k_2 d = 0 \quad (\text{VII-4a})
\]

for the trapped mode and

\[
k_1 \tanh k_1 t + k_2 \tanh k_2 d = 0 \quad (\text{VII-4b})
\]

for the trigonometric mode. The parameter \( t \) is the width of the well,
\( d = L - t \) where \( L \) is the thickness of the film, region 1 extends from
0 to \( t \), region 2 extends from \( t \) to \( L \), and \( k_1 = \sqrt{|E - V_1|}/D \). It was not
possible to match both experimental conditions; the values in Figure 46
give \( I_2/I_1 = 0.5 \) and \( H_1 - H_2 = 13 \text{ Oe} \). The resulting errors in the para­
meters \( t = 0.21 \mu m \) and \( V = 5.2 \text{ Oe} \) are 20%.

The linewidth of the resonance modes is a sensitive measure of the
impurity concentration. The addition of \( \text{Al}^{3+} \) into the lattice decreases
the linewidth; the presence of \( \text{Fe}^{2+} \) increases the linewidth. The
increase in \( \Delta H \) and its temperature dependence shown in Figure 42 indi­
cate that the production of oxygen vacancies is the more important
process occurring during the anneal. The temperature dependence of the
Figure 46. A schematic representation of the magnetic potential across the film thickness (0.56 μm). The substrate surface is to the right. The depth of the well is 5.2 Oe and its width is 0.21 μm. The amplitudes of the modes are arbitrary.
surface anisotropy can be pictured schematically by decreasing the well depth as the temperature is decreased, until at 180 K the internal fields are uniform and the surface mode becomes the uniform mode. As the temperature is decreased further, the well becomes a barrier and a surface mode is trapped at the substrate surface. Of the two sources of anisotropy connected with the presence of Fe$^{2+}$, i.e., a change in the magnetization relative to the bulk and the spin-orbit-lattice coupling, only the latter is expected to have a considerable temperature dependence. The magnetostriction due to Fe$^{2+}$ in YIG has been measured and has been found to increase smoothly as the temperature is decreased from the Curie temperature down to about 100 K (Hansen, 1977). The presence of Fe$^{2+}$ also affects the bulk crystalline anisotropy and the spin-wave resonance linewidth. These have also been measured as a function of Fe$^{2+}$ concentration and temperature (Hansen, et al., 1972). The increase in the linewidth at room temperature to 4.2 Oe gives a rough approximation to the Fe$^{2+}$ concentration of 0.024 per formula unit. For this concentration, the first crystalline anisotropy constant $K_1$ passes through zero (from negative values to positive values) at just above 200 K. This value of the Fe$^{2+}$ concentration corresponds to an O$^{2-}$ vacancy concentration of 0.014 per formula unit compared with a value for as-grown YIG of 6x10$^{-4}$ per formula unit (Metselaar and Larsen, 1976). It should be noted that the higher the O$^{2-}$ vacancy concentration, the more rapid is their diffusion (LeCraw, et al., 1977), which accounts for the width of the well produced by a surface reaction.
The surface anisotropy constants were calculated using Eq. (VII-2). The results are $K^S_{A (iso)} = -0.02 \pm 0.002$ and $K^S_{A (uni)} = -0.04 \pm 0.004$ erg/cm$^2$ and $K^S_{B (iso)} = -0.02 \pm 0.002$ and $K^S_{B (uni)} = 0.01 \pm 0.001$ erg/cm$^2$. It is expected that the larger change in anisotropy occurred at the free surface; then the first set of values belong to that surface.

C. Chromium on YIG

Cr was evaporated onto YIG samples from an electroplated rod in a bell-jar evaporator. The effect of this process on the perpendicular resonance spectrum of YIG is shown in Figure 47. The ratio $I_2/I_1$ has increased roughly two orders of magnitude over that of the control sample. The intensity of higher order modes is also increased. One Cr/YIG sample was etched in phosphoric acid at 85°C for 30 s, removing the Cr film. The spectrum returned to that of the control, giving an upper limit to the width of the interaction of 3 nm. Clearly, the interaction is more truly a surface one than those previously investigated. A critical angle at 300 K was found at $\zeta_C = 62^\circ$.

The perpendicular resonance spectrum of Cr/YIG samples was studied from 5 K to 400 K. The intensity ratio $I_2/I_1$ for the higher temperatures is shown in Figure 48. The interaction persists above 312 K; a Néel temperature of about $T_N = 430$ K is indicated by the data. This value is within the range previously reported for strained polycrystalline samples of Cr (see Chapter IV).

The field spacing between the first two modes is shown in Figure 49. There is an abrupt increase in the spacing at $T = 140$ K; on
Figure 47. The perpendicular resonance spectrum at 9.2 GHz and T = 300K for a Cr/YIG sample.
Figure 48. The temperature dependence of the relative intensities of the first two modes for Cr/YIG sample #31.
Figure 49. The separation of the first two modes in perpendicular resonance as a function of temperature for Cr/YIG.
either side of this temperature the spacing changes only very slowly.
To better understand what is happening to the film boundary conditions
around this critical temperature, it is necessary to examine the
intensity data for the lower temperatures, which is presented in
Figure 50. The curves are the least-squares fit to the data. There
is a broad minimum in the intensities of the even-numbered modes
centered at about $T = 120$ K. The position of this minimum suggests
that it is connected to the spin-flip transition in Cr; the width of
the transition is consistent with an elevated Néel temperature in the
Cr.

A schematic representation of these four modes is given in
Figure 51. The wider area represents YIG, and the narrower one, Cr.
The modes drawn are the amplitudes of the transverse magnetization,
which because the net magnetization aligns with the applied field
normal to the film, is actually out of the plane. Above $T_s$, Cr is in
the $AF_1$ state and $\vec{M}$ of the localized spins is perpendicular to the
applied field. The molecular field produced by the Cr magnetization
acts on the surface Fe$^{3+}$ spins, giving them an extra amplitude of
precession. As the temperature is lowered through the Cr spin-flip
region, there is an increase in the amount of Cr $AF_2$ ($\vec{M}$ parallel to the
applied field), and the pinning of the surface spins in YIG increases.
There is some % $AF_2$ where a linear YIG mode exists, with a minimum in
the intensities of the even-ordered modes. Below 60 K, the transition
to $AF_2$ in Cr is complete, and any further changes in the boundary
conditions (at either surface) are inherent in the YIG film. (The
Figure 50. The temperature dependence of the relative intensities of the first four modes for Cr/YIG sample #26.
Figure 51. A diagrammatic representation of the effect of Cr spins on the resonance modes of YIG.
Cr data below 50 K are discussed further in Section D).

It is clear from considering the room temperature critical angle of these samples and by examining Figure 8, that the surface spin-spin interaction can be adequately represented by a uniaxial surface anisotropy only. The surface anisotropy constants were calculated using Eq. (VII-2) and found to be $K_A^S(\text{uni}) = -0.02 \pm 0.006 \text{ erg/cm}^2$ and $K_B^S(\text{uni}) = 0.006 \pm 0.003 \text{ erg/cm}^2$ with the negative value identified as belonging to the Cr/YIG interface.

D. **Vanadium on YIG**

V was evaporated onto YIG in the bell-jar evaporator using a thin foil of V heated on a tungsten wire as the source. The resulting room temperature resonance spectrum is shown in Figure 52. As in the case of Cr/YIG, when the sample was etched for a short time in hot phosphoric acid, the spectrum returned to that of the control, indicating a sharp surface interaction.

Samples of V/YIG were studied as a function of angle from 300 K to 1.4 K. The temperature dependence of the critical angle is shown in Figure 53. There exists a critical temperature at $T = 50 \text{ K}$; it will be recalled that this temperature also corresponds to the maximum in linewidth of the resonance modes.

The field spacing between the first two modes as a function of temperature is seen in Figure 54. As in the case of the control sample, there are two distinct temperature regions. The rapid increase in $H_{1/2}$ below 40 K is due to the localization of a surface
Figure 52. The perpendicular resonance spectrum at 9.2 GHz and $T = 300K$ for a V/YIG sample.
Figure 53. The temperature dependence of the critical angle for V/YIG.

Figure 54. The spacing between the first two modes as a function of temperature for V/YIG.
mode which is present in the perpendicular resonance spectrum. That spectrum at 20 K is displayed in Figure 55. The intensity of the surface mode decreases rapidly as the mode becomes more localized. It is lost when the sample is immersed in liquid He.

Below the λ-point of liquid He, a surface mode appears in the parallel resonance spectrum. It is attributed to anisotropies located at the substrate surface.

The presence of a surface mode at room temperature in the V/VIG indicates that there is a significant surface interaction between the garnet and the metal. This coupling persists to the lowest temperatures studied, as seen in Figure 56. The behavior of the Cr/YIG sample essentially parallels that of the control; the increase in localization in the V/YIG sample is significantly larger. From Figure 57, it is seen that not only is the surface mode in the V/YIG sample more localized, but it is also more intense. It must be that the surface mode is caused by a chemical or physical defect in the garnet, and that the presence of V increases the number of these defects. Since the susceptibilities of V and Cr fine particles at low temperatures are nearly equal (Akoh and Tasaki, 1978), it is likely that the coupling involved is electronic rather than magnetic.

A possible source of the anisotropy present at the free surface of LPE-grown YIG films is the one-ion mechanism proposed by Rado (Rado, 1978). His is basically a reduced-symmetry argument, incorporating the assumptions that the surface layer consists of oxygen atoms (and thus that the bulk value of D applies to the underlying
Figure 55. The perpendicular resonance spectrum at 9.5 GHz and $T = 20$ K for V/YIG.
Figure 56. The spacing between the first two modes in perpendicular resonance for $T \leq 50K$ for the control, Cr/YIG and V/YIG samples.
Figure 57. Best-fit curves of the relative intensities of the first two modes for the control and V/YIG samples as a function of temperature.

Figure 58. The free surface anisotropy constant for the control and V/YIG samples as a function of temperature.
iron atoms), and that the surface is terraced so that the two chemically inequivalent planes of Fe$^{3+}$ parallel to an (001) surface alternate across the surface. His calculated values of $|K^S|$ are 0.007 erg/cm$^2$ at room temperature (which is correct to within experimental error) and 0.0115 erg/cm$^2$ at $T = 0$ K. The main objection to this approach is that its temperature dependence follows that of the garnet magnetization, which, as seen in Figure 4 and 16, is almost level in the region of interest. The one-ion mechanism undoubtable contributes to the anisotropy at the free surface, but it is not the dominant mechanism.

Another approach is suggested by considering a higher concentration of oxygen vacancies not only at the substrate surface, but also at the free surface (as grown). There are two modes of movement associated with an oxygen vacancy. The vacancies themselves may migrate; at the temperatures of the resonance experiments they are frozen (Metselaar and Larsen, 1976). Or electrons may transfer between Fe$^{3+}$ and Fe$^{2+}$, effectively smearing the position of the Fe$^{2+}$ around the oxygen vacancy.

The unquenched orbital angular momentum of Fe$^{2+}$ prefers to lie along a body diagonal. Thus, the octahedral sites which it occupies are no longer equivalent; there are four types of octahedral sites, each with its own preferred trigonal axis. At any temperature, there will be an increased energy associated with any magnetization orientation other than along a diagonal. At high temperatures, this energy can be minimized by redistributing the Fe$^{2+}$ ions to more
favorable sites when the orientation of the applied field is changed. Below about 50 K, the extra electrons of the Fe$^{2+}$ ions begin to be frozen in their most energetically favorable sites next to the oxygen vacancy (Mack and Smit, 1973). If Fe$^{2+}$ becomes more restricted to the surface region and tied to a particular trigonal direction below 50 K, then the surface anisotropy should increase and the surface mode become more localized as the temperature is decreased. However, all samples with increased Fe$^{2+}$ concentrations, annealed YIG samples (Yen, 1977), Al-reduced samples, and silicon-reduced samples (T. S. Stakelon, private communication), have a surface mode at parallel resonance, not at perpendicular resonance.

According to group theory (Cotton, 1971), an Fe$^{4+}$ ion in a tetrahedral site, which it prefers, is entirely equivalent to an Fe$^{2+}$ ion in an octahedral site. Those properties which depend on the details of the energy level diagram, such as magnetostriction and crystalline anisotropy, will remain unaltered if an increased concentration of Fe$^{4+}$ at the surface is considered instead of an increase in the amount of Fe$^{2+}$. With the change in species, it may then be possible that the surface mode would appear in the perpendicular resonance spectrum.

The intensity and field separation data suggest that the defect species at the surface is randomly spaced. As the film is removed from the LPE furnace, PbO may be deposited, resulting in an increased concentration of Pb$^{2+}$ on the free surface. These divalent ions would not be totally compensated for by Pt$^{4+}$, so the net result is to increase the Fe$^{4+}$ concentration relative to the bulk. Since the
films are thoroughly cleaned in acetic acid after growth and subjected to a short acid etch, the presence of Fe\(^{4+}\) would be associated with mechanical defects in the garnet surface.

In this model, the effect of the metal layer is to increase the number of Fe\(^{4+}\) ions. The intensity of the surface mode increases because the total number of spins precessing in that mode increases. The localization increases because as the number of Fe\(^{4+}\) ions on the surface increases, the average distance between them decreases, and the anisotropy field associated with the presence of each Fe\(^{4+}\) is reinforced by the neighboring ones. (Recall from Chapter II, Section C-6, that the decay length for a surface anisotropy goes as \(\sqrt{\phi/\rho}\), or about 11 nm for these experimental conditions.)

As seen in Chapter IV in the case of V, and as a general result (Teraoka and Kanamori, 1978), there is an increase in the density of states at the surface of transition metals. When brought into close contact, these metals may accept electrons from the garnet into their surface d-bands, thus changing the valency of Fe\(^{3+}\) to Fe\(^{4+}\).

Figure 58 presents the anisotropy constants for the control and V/YIG samples, calculated from Eq. (VII-2). The effect of V metallization is to more than triple the anisotropy at the free surface. The effect of Cr is smaller. What contribution there is from a magnetic interaction between V and Fe is difficult to assess. In Figure 56, the separation between the surface mode and the body mode in the V/YIG sample appears to become constant at about 8 K, a trend which is not seen in the control or Cr/YIG samples. Further
confirmation of this data and a comparison with other metal/YIG samples where there is a known magnetic transition in the metal in this temperature region are needed before a definite conclusion about the magnetic state of the V surface can be drawn.

E. Summary

The effect of the introduction of various magnetic and electronic interactions at the free surface of YIG on the spin-wave boundary conditions has been investigated using ferromagnetic resonance. The spectra were studied as a function of the angle of the applied field from 400 K to 1.4 K. The alterations were produced by a surface reduction of the garnet by Al, and by the evaporation of metallic Cr and V onto the film. The contributions of the isotropic and uniaxial terms to the free surface anisotropies (at room temperature) for these samples and the control were calculated and are presented in Table 3.

The room temperature free surface anisotropy constants at perpendicular resonance for the LPE-grown control YIG sample agree with other published values (Vittoria and Schelleng, 1977), within experimental error. The value of the anisotropy constant at low temperatures (T < 10 K) agrees within experimental error to a theoretical zero temperature result (Rado, 1978). The theoretical model does not account for the exhibited temperature dependence of the free surface anisotropy. A calculation was presented which predicted that a surface mode localized at the substrate surface and due to the diffusion of Gd$^{3+}$ and Ga$^{3+}$ into the magnetic garnet should not be
Table 3. The Isotropic and Uniaxial Contributions to the Free Surface Anisotropy at Room Temperature.

<table>
<thead>
<tr>
<th></th>
<th>$K^S_{(iso)}$ erg/cm$^2$</th>
<th>$K^S_{(uni)}$ erg/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-0.002±0.003</td>
<td>+0.008±0.003</td>
</tr>
<tr>
<td>Al/YIG</td>
<td>-0.02±0.002</td>
<td>-0.04±0.004</td>
</tr>
<tr>
<td>Cr/YIG</td>
<td>0</td>
<td>-0.02±0.006</td>
</tr>
<tr>
<td>V/YIG</td>
<td>+0.002±0.002</td>
<td>-0.03±0.005</td>
</tr>
</tbody>
</table>
seen even at the lowest temperatures attained here. A surface mode was
found at parallel resonance at $T = 1.4$ K. It was postulated that the
effective width of the diffusion region was increased by the inclu-
sion of $\text{Pb}^{2+}$ into the garnet lattice at the substrate surface, and a
surface mode was then trapped in the potential well.

The reduction of the garnet by $\text{Al}$ resulted in a region about
$0.2$ pm thick near the free surface which had an increased concentra-
tion of $\text{Fe}^{2+}$ relative to the bulk. The increase in magnetization,
magnetostriction and crystalline anisotropy due to the $\text{Fe}^{2+}$ create an
effective magnetic potential well at the free surface. The trapped
surface mode is seen in parallel resonance. As the temperature is
decreased, the magnetostriction and the crystalline anisotropy
increase, until at $180$ K, the internal fields in the film are
uniform, and the surface mode has become the uniform mode. Below
$180$ K, $\text{Fe}^{2+}$ creates a potential barrier which traps a surface mode at
the substrate surface. There is no temperature dependence of the
critical angle in these samples.

The effect of $\text{Cr}$ on the free surface of $\text{YIG}$ was to produce a
surface mode in perpendicular resonance. The surface interaction
is magnetic and limited to the first $3$ nm of the $\text{YIG}$ film. The
magnetic transitions in $\text{Cr}$ were identified in the spectra. The
spectrum returned to that of the control at about $T = 430$ K; there
was a broad minimum in the intensity of the even-ordered modes
centered at about $T = 120$ K. An elevated Néel temperature and a
broadened spin-flip transition are characteristics of polycrystalline, strained samples of Cr.

The data of the V/YIG samples were the most difficult to interpret. The temperature dependence closely followed that of the control, but below 50 K, the surface mode was both more localized and more intense compared with the control. It was suggested that this surface mode was due to the presence of \( Fe^{4+} \) randomly situated on the surface. The presence of V may increase the number of \( Fe^{4+} \) ions on the surface by accepting electrons from \( Fe^{3+} \) into its surface d-band.

A magnetic transition in the surface of V could not be absolutely identified. A levelling of the value of the field separation in the V/YIG samples at about 8 K, a behavior not seen in the control or Cr/YIG samples, hints at such a transition. A transition temperature of 8 K agrees with a previously reported value (Akoh and Tasaki, 1978) within their experimental error. Further work in the temperature range below 50 K is needed to make such an assignment certain. Promising candidates for evaporation onto YIG are the alloys of nickel and copper. The ferromagnetic transition temperature of NiCu can be continuously adjusted downward by increasing the amount of Cu. Samples with a high percentage of Cu also do not have the disadvantage of the very large magnetostriction of Ni. Comparison of data from these types of samples with that of V/YIG should elucidate the meaning of the data below 10 K.
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