FERROMAGNETIC RESONANCE STUDY OF SPINTRONICS MATERIALS

DISSERTATION

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

By

Yurii N. Bataiev, B.S.

*****

The Ohio State University
2008

Dissertation Committee:
Professor Arthur J. Epstein, Advisor
Professor Fengyuan Yang
Professor Lei Bao
Professor David G. Stroud

Approved by

______________________________
Advisor

______________________________
Physics Graduate Program

______________________________
Advisor
ABSTRACT

The search for the materials useful for spin-based electronics (spintronics) has been a very important part in the developing of spintronics technology and spin-based electronic devices. Organic-based semiconductor ferromagnets are a class of materials which have unique combination of properties suitable for sources or analyzers of spin-polarized currents are being studied by using different techniques as candidates for spintronics applications. Spintronics devices are starting to impact high-technology industries and could create new multibillion dollar industries which we could not always predict.

Ferromagnetic Resonance (FMR) technique along with other experimental methods are used to study a number of ferromagnetic semiconductors to get information about their chemical and crystal structure, surface and bulk properties, main parameters related to the conductivity and spins of the electrons.

This dissertation investigates temperature- and structure-dependent behavior of different generations of magnets $V[TCNE]_x$ and $V_xCo_{1-x}[TCNE]_2$ (TCNE is tetracyanoethylene). The obtained data have been analyzed using famous models for FMR in semiconductors.
ACKNOWLEDGMENTS

It is my pleasant duty to record my gratitude to my scientific and academic adviser, Professor Arthur J. Epstein. I wish to thank Dr. Arthur J. Epstein for his constant support and patience. His kind work brought me to the proper level of knowledge and proficiency required for the excellent research specialist.

I am indebted to Dr. Raju Nandyala for the interesting work we did together and for introducing me the field of study I was developing for many recent years. I am also deeply grateful to Dr. Konstantin I. Pokhodnya for providing a number of samples used in my experiments. I would like to thank all other members of Professor Epstein’s group for theirs assistance and friendship. Above all, I am grateful to Dr. Vladimir N. Prigodin for very useful discussions and for the benefit I got from his criticism of my work.

I want to acknowledge support provided in part by different U.S. organizations without which this dissertation could not have been written: Department of Energy, Army Research Office and Defense Advanced Research Projects Agency.

And, finally, I want to thank my parents, Mr. Nickolay I. and Ms. Yevgeniya L. Bataiev for their encouragement, help and much more. My special thanks go to my brother Nick. I thank you my friends for invaluable support during these years.
VITA

March 28, 1977………………………. Born - Kiev, Ukraine

1994 -1999……………………………  B.S. Physics, Moscow Institute of Physics and Technology, Dolgoprudny, Russia

1999 -2000……………………………  Department Fellowship Scholar, Department of Physics, The Ohio State University, Columbus, OH

2000 -present………………………….  Graduate Teaching and Research Associate, The Ohio State University, Columbus, OH

FIELDS OF STUDY

Major Field: Physics

Studies in:

   Experimental Condensed Matter Physics
   - Magnetism and Magnetic Materials

Professor Arthur J. Epstein
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</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 Figures</td>
<td>.vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Theoretical Background</td>
<td>4</td>
</tr>
<tr>
<td>3. Experiment</td>
<td>24</td>
</tr>
<tr>
<td>4. FMR study of film samples</td>
<td>32</td>
</tr>
<tr>
<td>5. Conclusions</td>
<td>44</td>
</tr>
<tr>
<td>Appendix: Additional Figures and Table</td>
<td>45</td>
</tr>
<tr>
<td>Bibliography</td>
<td>55</td>
</tr>
</tbody>
</table>
List of Figures

**Figure 1.** Diagram of the EPR instrument. [From Ref. 2] .................. 2

**Figure 2.** Coordinate system used in this paper. The orientation of $H$ is given by $(\theta_H, \phi_H)$; the orientation of $M$ is described by $(\theta, \phi)$. [From Ref. 2] .................. 2

**Figure 3.** FMR spectra of Ga$_{0.98}$Mn$_{0.02}$As sample at $T = 10$ K. $\theta_H$ changes from 0$^0$ to 90$^0$ for geometry 2. Full circles correspond to FMR positions. Microwave magnetoconductivity changes in the samples cause variations in the absorption signal for low fields when $\theta_H$ is less then 30$^0$. [From Ref. 2] .................. 6

**Figure 4.** Angular dependence of the FMR fields. Panel 1 corresponds to geometry 1; panel 2 and 3 correspond to geometry 2 and geometry 3 respectively. The solid curves represent theoretical fit to the $H_r$ (FMR positions). All three dependences are very different. [From Ref. 2] .......................................... 7

**Figure 5.** Frequency dependence of the linewidth for bulk ferromagnets. The parameters $\{G(10^{-8} s^{-1}), g, \mu_0 M(T=0)\}$ for materials are: Fe $\{0.084, 2.09, 2.187 T\}$, Co $\{0.3, 2.16, 1.759 T\}$, Ni $\{0.245, 219, 0.641 T\}$, Gd $\{0.2, 1.97, 2.589 T\}$. $\Delta H_{inhom} = 1$ mT is small. [From Ref. 1] .......................................................... 10

**Figure 6.** (a) Angular dependence of the $\Delta H_{pp}$ for Ga$_{0.97}$Mn$_{0.03}$As/GaAs as a function of $\phi_H$ geometry 3 in left panel and as a function of $\theta_H$ geometry 1 in right panel. (b) Temperature dependence of $\Delta H_{pp}$ for $H \parallel [001]$, $H \parallel [110]$, $H \parallel [100]$. [From Ref. 2].

**Figure 7.** a) SWR of Ga$_{0.924}$Mn$_{0.076}$As at 4K for three different films; b) SWR for 150 nm thick film of Ga$_{0.924}$Mn$_{0.076}$As at 4K and at 40 K. [From Ref. 2] .................. 14

**Figure 8.** Power absorption in thick plates. The ratio of $T_D/T_2$ is different. [From Ref. 21] ........................................................................................................ 16

**Figure 9.** Derivative of the power absorption in thick plates with different ratios of $T_D/T_2$. [From Ref. 21] .......................................................... 16

**Figure 10.** $\gamma(\delta H)T_2$ and $\gamma(\Delta H)T_2$ dependence on $(T_D/T_2)^{1/2}$ for the power absorption in thick plates. [From Ref. 21] .......................................................... 19
Figure 11.  $\gamma(\Delta H)T_2$ and $\gamma(\delta H)T_2$ dependence on $(T_D/T_2)^{1/2}$ for the derivative of the power absorption in thick plates. [From Ref. 21] ........................................ 19

Figure 12.  $A/B$ dependence on $(T_D/T_2)^{1/2}$ for the power absorption in thick plates. [From Ref. 21] ......................................................... 20

Figure 13.  $A/B$ dependence on $(T_D/T_2)^{1/2}$ for the derivative of the power absorption in thick plates. [From Ref. 21] ............ 20

Figure 14.  Electron spin resonance in small 5 microns in diameter sodium particles. [From Ref. 21] ....................................................................................... 22

Figure 15(a, b, c).  Electron spin resonance of lithium thick plates for different $T_D/T_2$: 0.12, 0.034 and 0.003 (for a, b and c respectively). [From Ref. 21] .............. 22

Figure 16.  The asymmetry parameter $A/B$ for different ratios $T_D/T_2$. [From Ref. 21] ....................................................................................... 22

Figure 17.  The electron spin resonance absorption in the range of the completely anomalous skin effect (theory). [From Ref. 21] ........................................ 22

Figure 18. ........................................................................................................ 34

Figure 19 ........................................................................................................ 36

Figure 20 ........................................................................................................ 38

Figure 21 ........................................................................................................ 39

Figure 22. ........................................................................................................ 41

Figure 23 ........................................................................................................ 42

Figure 24 ........................................................................................................ 43

APPENDIX

Figure 1 ........................................................................................................ 45

Figure 2 ........................................................................................................ 46

Figure 3 ........................................................................................................ 47
Figure 4 ........................................................................................................... 48
Figure 5 ........................................................................................................... 49
Figure 6 .......................................................................................................... 50
Figure 7 .......................................................................................................... 51
Figure 8 .......................................................................................................... 52
Figure 9 .......................................................................................................... 53
List of Tables

Table 1 .................................................................................................................. 54
Chapter 1

Introduction

Ferromagnetic resonance (FMR) is a very powerful experimental technique in the study of ferromagnetic thin films [1]. It allows us to measure all the most important parameters of the material: Curie temperature, total magnetic moment, parameters of the relaxation process of magnetization and others.

In this paper, the example of the analysis done by FMR technique will be given using the data obtained from the standard 9.4 GHz (X-band) Bruker electron paramagnetic resonance (EPR) spectrometer. Figure 1 shows a typical FMR set up: the applied DC magnetic field is horizontally oriented and the small rf-microwave magnetic field is in the vertical direction [2]. The sample holder tube containing the film is inserted into a liquid helium continuous flow cryostat which can cool the sample to 4K. During the experiment, the DC magnetic field changes, while the microwave frequency is fixed. Under the resonance conditions the precession of the total magnetic moment around the local magnetic field $H_{eff}$ takes place.
Let us consider the Landau-Lifshitz-Gilbert equation of motion which describes the time evolution of the magnetization around the equilibrium position [1, 2]

\[
\frac{d \vec{M}}{dt} = -\gamma [ (\vec{M} \times (\vec{H} + \vec{H}_{\text{eff}}) ) ] + \frac{G}{\gamma \cdot M} \left( \vec{M} \times \frac{\partial \vec{M}}{\partial t} \right)
\]

(1)

where \( \vec{H} \) is the externally applied DC magnetic field, \( \vec{H}_{\text{eff}} \) is the effective magnetic field which combines (rf-) magnetic field \( \vec{h}(t) \) with frequency \( \omega/2\pi \), the demagnetizing field, and the magnetocrystalline anisotropy field. \( G \) represents the Gilbert damping parameter and \( \gamma = g\mu_B/\hbar \) is the gyromagnetic ratio. \( g \) is the spectroscopic splitting factor, for a free electron \( g = 2.0023 \).
One of the main goals of this paper is to demonstrate the advantages and limits of the ferromagnetic resonance technique. First, the analysis of the angular dependence of the FMR field will be given. Second, the angular and temperature dependences of the FMR linewidth will be discussed. Then the concepts of the Gilbert damping parameter and spin waves will be presented, with main focus placed on the discrepancies between the theory and the experiment. At the end of the paper, the electron diffusion and the Dysonian effect will be reviewed.
Chapter 2

FMR field angular dependence

Equation (1) is the fundamental equation of the ferromagnetic resonance. It is possible to analyze the resonance frequency of the FMR by neglecting the second term in the right part of that equation and assuming that deviations from equilibrium are small. The resonance condition for any field orientation can be expressed in the spherical coordinates [1, 3] as:

\[
\omega_{\text{res}} = \frac{\gamma}{M \sin \theta} \left[ \frac{\partial^2 F}{\partial \theta^2} \frac{\partial^2 F}{\partial \varphi^2} - \left( \frac{\partial^2 F}{\partial \theta \partial \varphi} \right)^2 \right]^{1/2},
\]

where \( F \) is the free energy density, and \( \theta \) and \( \varphi \) are polar angles for the magnetization orientation.

Equation (2) works well in the analysis of magnetic anisotropy of the III\(_{1-x}\)Mn\(_x\)V ferromagnetic semiconductors (FMSs). III\(_{1-x}\)Mn\(_x\)V materials are candidates for spintronic devices due to their magnetic anisotropy. Let’s use Ga\(_{1-x}\)Mn\(_x\)As layer (shown in figure 2) for further investigation. If we consider a thin film with tetragonal symmetry (\( a=b\neq c \), \( \alpha=\beta=\gamma=90^0 \)) in the applied magnetic field \( H \), we will get the following expression [1, 4] for the free energy density:
\[ F = \frac{1}{2} M \left\{ -2H \left[ \cos \theta \cos \theta_H + \sin \theta \sin \theta_H \cos(\phi - \phi_H) \right] + 4\pi M \cos^2 \theta - H_{2\perp} \cos^2 \theta \right\} \]
\[ -\frac{1}{2} H_{4\perp} \cos^4 \theta - \frac{1}{2} H_{4\parallel} \frac{1}{4} \left( 3 + \cos 4\phi \right) \sin^4 \theta - H_{2\parallel} \sin^2 \theta \sin^2(\phi - \frac{\pi}{4}) \right\} \]  

In the above formulae \(H_{2\parallel}\) and \(H_{4\parallel}\) correspond to the in-plane uniaxial and in-plane cubic anisotropy fields; \(H_{2\perp}\) is the perpendicular uniaxial field, and \(H_{4\perp}\) is the perpendicular cubic anisotropy field. There is a simple relationship between anisotropy fields and the anisotropy energies in the above equation: \(H_i = 2K_i/M\). The first term in the right part of the equation (3) corresponds to the Zeeman energy, the second term is the demagnetization energy, and the last part is related to the magnetic anisotropy energy. If we consider equations (1)-(3) and take into consideration the minimization of the free energy density by \(\theta\) and \(\phi\) (\(\partial F/\partial \phi = 0\) and \(\partial F/\partial \theta = 0\)), we can get the applied field at resonance frequency [2]. The general formula for applied field is very long, even for the specific orientations. That is why these formulae are omitted and only fitted EPR parameters obtained from the fit of the solution equations will be discussed. As an example, let us choose three high symmetry orientations which will be called geometry 1, geometry 2 and geometry 3. Geometry 1: \(H\) and \(M\) are in the (110) plane (\(\phi = \phi_H = 45^\circ\)). Geometry 2: \(H\) and \(M\) are in the (010) plane (\(\phi = \phi_H = 0^\circ\)). For geometry 3 vectors \(H\) and \(M\) are in the (001) plane (\(\theta = \theta_H = 90^\circ\)).

Let us consider FMR angular dependence for Ga_{1-x}Mn_xAs sample (x = 0.02) [24].
Figures 3 and 4 show FMR spectra for representative sample as a function of applied field orientation at $T = 10$ K. The angles are taken relative to the axes of the crystal. In Figure 3 the FMR peak positions are indicated by red circles. Figure 4 has three panels, and each panel shows the angular dependence of $H_R$ for one of the three geometries.

**Figure 3.** FMR spectra of Ga$_{0.98}$Mn$_{0.02}$As sample at $T = 10$ K. $\theta_H$ changes from $0^\circ$ to $90^\circ$ for geometry 2. Full circles correspond to FMR positions. Microwave magneto-conductivity changes in the samples cause variations in the absorption signal for low fields when $\theta_H$ is less then $30^\circ$. [From Ref. 2]
Figure 4. Angular dependence of the FMR fields. Panel 1 corresponds to geometry 1; panel 2 and panel 3 correspond to geometry 2 and geometry 3 respectively. The solid curves represent theoretical fit to the $H_r$ (FMR positions). All three dependences are very different.
[From Ref. 2]
The procedure for getting magnetic anisotropies consists of the following steps [2]:

1. At the beginning \( g = 2.00 \). The data in panel 3 is fitted to the equation of the resonance field. 2. The approximate values of \( 4\pi M_{\text{eff}}, H_4\parallel \) and \( H_2\parallel \) from step 1 are used for nonlinear least squares fit to the FMR positions for data presented in panels 1 and 2. During this step, the three parameters \( g, 4\pi M_{\text{eff}}, \) and \( H_{4\perp} \) can be changed. 3. Iteration is performed in which the new \( g \)-value is used now. Repetition of the procedure from step 1 occurs to obtain new values for \( 4\pi M_{\text{eff}}, H_4\parallel \) and \( H_2\parallel \). The iterations should be performed until five parameters \( 4\pi M_{\text{eff}}, H_{4\perp}, H_4\parallel, H_2\parallel \) and \( g \) reach equilibrium value.

For the Ga_{0.98}Mn_{0.02}As specimen the above analysis gives the following values:

\[
4\pi M_{\text{eff}}=2083\pm64 \text{ Oe}, \quad H_{4\perp}=1826\pm78 \text{ Oe}, \quad H_4\parallel=1985\pm71 \text{ Oe}, \quad H_2\parallel=608\pm80 \text{ Oe}, \quad \text{and} \quad g=1.87\pm0.02.
\]

### 2.1. FMR linewidth (angular and temperature dependences)

The peak-to-peak FMR linewidth \( \Delta H_{pp} \) is an important parameter in measuring the relaxation rate of the magnetization [2]. Two factors determine FMR linewidth. The first one is the intrinsic relaxation of system magnetization, the so called Gilbert damping. The second parameter corresponds to the magnetic inhomogeneities of the ferromagnetic film. Both of these factors were not studied well for III_{1-x}Mn_{x}V alloys. In this investigation \( \Delta H_{pp} \) of Ga_{1-x}Mn_{x}As will be measured as a function of temperature, and
then as a function of applied field orientation. The general formula for the linewidth is given by the expression [1, 5]: $\Delta H_{pp} = \Delta H_{in\text{hom}} + \Delta H_{\text{hom}}$. According to Suhl [6] the intrinsic contribution to the FMR linewidth is angular dependent and can be written in the form

$$\Delta H_{\text{hom}} = \frac{2}{\sqrt{3}} \frac{1}{| \partial \omega_{\text{res}} / \partial H |} \frac{G}{M^2} \left( F_{\theta \theta} + \frac{F_{\phi \phi}}{\sin^2 \theta} \right) \approx \frac{2}{\sqrt{3}} \frac{G}{\gamma^2 M} \omega$$  (4)

where $G$ is temperature-dependent. It also depends on wavevector, and could manifest anisotropy [7, 8]. We can say that on the microscopic level, the viscous damping of the magnetization happens and ‘friction’ of the system is proportional to the ‘precession rate’. The experimental evidence that supports formula (4) is shown in figure 4 for Fe, Co, Ni and Gd. The angular-dependent $\Delta H_{\text{hom}}(\theta, \phi)$ has minima at principal axes and it has maxima where the direction of the magnetization changes significantly. It has to be mentioned that in the above equations the Gilbert damping parameter is considered to be constant. The anisotropy of the Gilbert parameter can be very large. For example, the measurements along the easy axis are 30% and 50% different from measurements along the hard axis for Fe and fcc Co samples respectively [8, 9]. This fact can be explained in the following way: if the precession of the magnetization happens around the hard axis, it is less damped since it goes in the favorable direction.
ΔHpp exhibits a strong angular dependence on the angle between the field orientation and crystal axes similar to the FMR field position. The angular dependence of Ga0.97Mn0.03As/GaAs 300 nm thick is shown in figure 5a. On the left panel the dependence is given for geometry 3 and on the right panel for geometry 1. The strong dependence of linewidth on orientation of the field (for geometry 3 it changes 3 times) implies that inhomogeneities in the ferromagnetic films play a significant role in the FMR broadening [10]. If the field is applied at some angle between the easy and the hard axes, the shape of the resonance spectrum will be different from pure Gaussian or pure
Lorentzian, which makes the study of $\Delta H_{pp}$ very complicated. This is the situation when the sweep of the magnetic field changes the orientation of the magnetization.

Figure 5(b) shows the temperature dependence of the linewidth for three different orientations of the field (which is typical for all Ga$_{1-x}$Mn$_x$As/GaAs samples). The linewidth stays constant mostly in the region where the sample is ferromagnetic, and then increases drastically after passing the Curie temperature. This may be understood from the point of view that spin disorder becomes very high in the ferromagnetic-paramagnetic and paramagnetic regions.

The FMR linewidth inhomogeneous broadening happens mostly because of the sample’s mosaicty and defects. Other sample imperfections contribute to inhomogeneous broadening. $\Delta H_{pp}$ becomes especially large in the case of the coupling of the uniform mode to the spin waves [11]. The inhomogeneous broadening can be written in the form [10]:

$$\Delta H_{in\ hom} = \Delta H_0 + \Delta \theta \frac{\delta H_r}{\delta \theta_h} + \Delta H_{int} \frac{\delta H_r}{\delta H_{int}}$$  \hspace{1cm} (5)

$\Delta H_0$ corresponds to random angular-independent distribution of defects and intrinsic damping. The second term is related to small variations in the orientation of anisotropy axis around the film normal. The last term is just a distribution of $\Delta H_{int}$ in the internal field $H_{int}=4\pi M+(2K_2/M)+(4K_4/M)$. 

11
The Gilbert damping parameter

The Gilbert damping parameter corresponds to the ‘viscous’ damping of the magnetization motion [2]. It characterizes collective magnetization dynamics of the ferromagnets, as shown in equations (1) and (4). First theories of magnetization dynamics for transition metals considered exchange coupling ($\propto S \cdot s$) as a main relaxation mechanism [12, 13]. $S$ stands for localized d-shell spins and $s$ corresponds to the itinerant s-p band carrier spins. It appeared later that d-electrons also show itinerant behaviour. The p-d exchange-coupling between the itinerant holes and localized moments plays an important role in the damping of Ga$_{1-x}$Mn$_x$As systems. The damping process is divided into two steps. In the first step, the annihilation of the spin wave happens by the p-d exchange interaction of the local-moment magnon and hole which has a spin flip. In the second step, the relaxation of the itinerant hole spin happens through spin-orbit interaction [14]. In the microscopic theory given by Sinova et al in [14] Gilbert damping parameter depends on Mn-moment density, spin hole lifetime, and hole concentration.

The Gilbert damping parameter depends, first of all, on spin-orbit interaction. There is the following relationship between the $G$ parameter and g-factor of the Mn-ion/hole complex [15]:

$$G \propto (g - 2)^2 \sim \lambda^2 = \left(\frac{Z}{137}\right)^2$$

(6)
2.2. Spin Waves in Ferromagnets

The FMR spectra discussed above, relates to the uniform precession, for which at any moment all magnetic moments are parallel to each other in the whole film. This is the so-called spin wave mode with wave vector $k=0$. In general, magnetization does depend on space and time, when magnons are excited. The excitation usually happens by thermal or by mechanical means. Spin waves satisfy standing wave conditions, and boundary conditions of the film, and can be seen as a series of additional peaks in FMR spectra (see for example figure 6). The peaks contain a lot of information about the exchange energy [16].

Spin waves depend on the geometry of the experiment. There are three different types of spin waves regimes [17]: a) linear dispersion regime up to $200 \text{ m}^{-1}$ (wavelength greater than 3 cm); b) magnetostatic modes regime up to $10^7 \text{ m}^{-1}(600 \text{ Å})$ with flat dispersion and c) a spin-wave regime above $10^7 \text{ m}^{-1}$. Here, the focus will be made on the SWRs in Ga$_{1-x}$Mn$_x$As films and also on what happens with the spin waves if thickness of the film or temperature changes.

Figure 6 shows the SWR spectra for Ga$_{0.924}$Mn$_{0.076}$As films with Curie temperature 65 K and with different thicknesses: 100, 150, and 200 nm [18]. The applied field was normal to the film plane, because that is the case of the best SWR resolution. The uniform FMR mode appears around 8 KOe and with all other SWR modes at lower fields. The thick sample shows seven resonances. In figure 6a, it is easy to see that the separation between SWR modes are getting larger as the thickness decreases.
The separation between the SWR modes also increases as temperature decreases, which happens either because of 1) the change in the magnetization or 2) the change in the magnetic anisotropy fields.

The spin waves shown in figure 6 have linear dependence for separation between the modes: \( H_n \sim n \). Goennenwein et al [19] show similar spectra with \( H_n \sim n^{2/3} \). The Kittel pinning model for thin ferromagnetic films gives the quadratic dependence for the distances between resonance fields: \( H_n \sim n^2 \). The phenomenon of SW dispersion corresponds to the dependence of the magnetic parameters of the film on the distance \( x \) from the interface. The analysis done by experimental and theoretical means [19, 20]

![Figure 7. a) SWR of Ga\(_{0.924}\)Mn\(_{0.076}\)As at 4K for three different films; b) SWR for 150 nm thick film of Ga\(_{0.924}\)Mn\(_{0.076}\)As at 4K and at 40 K. [From Ref. 2](image)
strongly suggests that anomalous SW dispersion is due to a gradient in uniaxial anisotropy and spin stiffness and only after that due to variation of the magnetization. This phenomenon needs to be investigated further to make final conclusions. Experimental results are explained mostly by variations in the linear [19] or a quadratic [20] dependence on the distance x from the interface Ga$_{1-x}$Mn$_x$As/GaAs.

### 2.3. Electron diffusion and the Dysonian lineshape

Let us consider the theory and experimental results of the electron diffusion and the Dysonian lineshape. Following parameters appear in the Dyson’s theory [21]: $T_D$ corresponds to the time necessary for the electron to diffuse through the skin depth. $T_1$ is the electron spin relaxation time. In case of metals we have $T_1=T_2$. $T_T$ is the time required for the electron to traverse the sample. The first case is $T_T<<T_D$, which is the equivalent to the film with a small thickness compared to the skin depth [21]:

$$P = \frac{\omega H_1^2}{4}(V)\omega_0 \chi_0 T_2 \frac{1}{1 + (\omega - \omega_0)^2 T_2^2}$$

where $V$ is the volume of the sample, $H_1$ is the amplitude of the linearly polarized rf magnetic field, $\chi$ is the paramagnetic part of the static susceptibility, and $\omega_0$ is the resonant frequency. In this case, the absorption does not depend on diffusion and has a Lorentzian profile. The half width is $1/T_2$. 

15
Another very important case is when $T_1 \gg T_D$ and $T_T \gg T_2$. These conditions are realized for thick samples. The result for an arbitrary ratio of $T_D/T_2$ is given by the formula:

$$P = -\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi o T_2\right] \frac{T_D}{2T_2} \times \left\{ \frac{R^4 (x^2 - 1) + 1 - 2 R^2 x}{[(R^2 x - 1) + R^4]^2} \right\} \times \left[ \frac{2\xi}{R(1 + x^2)^{1/2}} + R^2 (x + 1) - 3 \right] + \frac{2 R^2 - 2 x R^4}{[(R^2 x - 1)^2 + R^4]^2} \times \left[ \frac{2 \eta}{R(1 + x^2)^{1/2}} + R^2 (x - 1) - 3 \right],$$

where $x = (\omega - \omega_0) T_2$, $\xi = \text{sign of } x[(1 + x^2)^{1/2} - 1]^{1/2}$, $\eta = [(1 + x^2)^{1/2} + 1]^{1/2}$, $R = (T_D/T_2)^{1/2}$, $\delta = c/(2\pi\sigma\omega)^{1/2}$ is the classical skin depth and $A$ is the area of the surface.

**Figure 8.** Power absorption in thick plates. The ratio of $T_D/T_2$ is different. [From Ref. 21]

**Figure 9.** Derivative of the power absorption in thick plates with different ratios of $T_D/T_2$. [From Ref. 21]
Figure 7 shows plots of equation (8) for different ratios of $T_D/T_2$. The derivative of the power absorption is plotted on figure 8. Three critical cases are easier to handle than equation (8). These cases are:

1. $T_T >> T_D; T_T >> T_2; T_D/T_2 \to 0$.
   
   This is the case of the metals with high conductivity at low temperatures. The absorption lines are narrow.

2. $T_T >> T_D; T_T >> T_2; T_D/T_2 << 1$.
   
   The second case is similar to the first one, with the only difference in the ratio $T_D/T_2$.

3. $T_T >> T_D; T_T >> T_2; T_D/T_2 >> 1$.
   
   The third case is the case of the thick plate with slowly diffusing magnetic dipoles. The nuclei are nearly stationary, and would also be the case of paramagnetic impurities spread in the volume of the sample.

It is possible to get a lot of useful information by using the Dysonian theory [21]. For example, it allows us to determine the $g$-values from figures 9 and 10. It also shows how the relaxation time $T_2$ can be determined by using the points of the half-power absorption. Figures 11 and 12 represent the dependence of the ratio $T_D/T_2$ on the asymmetry of the lineshape $(A/B)$. The asymmetry parameter $(A/B)$ will be used to compare the theory and the experiment.

The importance of surface relaxations was determined by comparing the linewidth of dispersed sodium and dispersed lithium with bulk samples. The skin depth of Na at 296 K and when $f=300$ Mc/s is 6$\mu$m, and the skin depth of Li under same conditions is 8$\mu$m. The size of the particle in any dispersion was less then 5$\mu$m. The skin depth at $f=320$
Mc/s is larger than the particle’s size. For this case, the theoretical curve is given by the derivative of equation (7). Figure 13 shows the experimental signal from the sodium dispersion and the theoretical curve. The agreement between both of them is very good. The relaxation time found from the curve is $T_2=6\times10^{-9}$ s. For the bulk metal, the result for the relaxation time is $T_2=9\times10^{-9}$ s. The difference between the two numbers is within the normal range of relaxations times, which can be found in different samples. If the measured difference was due to the surface effect, we would get surface relaxation time around $2\times10^{-8}$ s. The surface relaxation time has no effect on the lineshape in thick samples and will not be considered in analysis. For bulk Li, surface relaxations are insignificant, and Li relaxation time is $2\times10^{-8}$ s.

Let us consider the experimental results in Li. Figure 14 shows spectra with different ratios $T_D/T_2$. It is easy to see that when $T_D/T_2$ is getting smaller, the right peak of the derivative spectrum becomes small and then disappears completely. This fact is in very good agreement with the Dyson’s theory shown on figure 8.

The ratio $A/B$ could change from 2.7 to 19, and is easily changed by varying the temperature of the sample.

The comparison of the theoretical and the experimental data is shown in figure 15. It should be mentioned that a lot of experimental data are shifted to the left of the theoretical curve. The explanation for this is that surface irregularities stop the diffusion of the electrons, and as a result, $T_D$ is getting larger. The sodium sample had a very smooth surface, its points lie very close to the theoretical curve. It was prepared by
special technique: molten sodium was poured between two glass cylinders. The Be sample also had a very smooth surface and it lies practically on the curve.

If the ratio A/B is known, then it is possible to find the diffusion time of the electrons.

**Figure 10.** $\gamma(\delta H)T_2$ and $\gamma(\Delta H)T_2$ dependence on $(T_D/T_2)^{1/2}$ for the power absorption in thick plates. [From Ref. 21]

**Figure 11.** $\gamma(\Delta H)T_2$ and $\gamma(\delta H)T_2$ dependence on $(T_D/T_2)^{1/2}$ for the derivative of the power absorption in thick plates. [From Ref. 21]
For the case when mean free pass $\Lambda$ is very small compared with the skin depth, and is assumed that the velocity $v$ of all the electrons is the same, the expression for the diffusion time is $T_D = \frac{3\delta^2}{2v\Lambda}$. The conductivity is given by $\sigma = Ne^2\Lambda/m^*v$. That is why we can express the diffusion time as $T_D = \frac{3}{2} (\delta^2 Ne^2/\sigma)(1/m^*v^2)$. If we take the observed ratio $A/B$ for beryllium, we will get $m^*v^2/2 = 16\pm 2\text{eV}$. For the free electron ($m^*/m=1$) the calculations give 14.3 eV.

![Figure 12](image1.png)

**Figure 12.** $A/B$ dependence on $(T_D/T_2)^{1/2}$ for the power absorption in thick plates. [From Ref. 21]

![Figure 13](image2.png)

**Figure 13.** $A/B$ dependence on $(T_D/T_2)^{1/2}$ for the derivative of the power absorption in thick plates. [From Ref. 21]
The A/B is also very important, because it allows us to distinguish the resonance due to impurities. In the case of stationary paramagnetic impurities distributed on the surface the ratio A/B=1. If the impurities are distributed within the volume of the sample, then the A/B ratio depends on the profile of the line. If the spectrum has a Lorentzian profile then A/B=2.7; if it is Gaussian, then A/B=2.0. In thick samples the ratio A/B can not be 1.0 or 2.0 for conduction electrons. A/B=2.7 happens only in very few cases when diffusion is very slow.

We have the classical case when the mean free path of the electrons is much smaller than the skin depth. The field penetration is controlled by the skin depth parameter \( \delta=(c^2/2\pi\sigma\omega)^{1/2} \). When the classical conditions are not met, then the field penetration is controlled by \( \Lambda \) and this is the case of “anomalous skin effect”. For example, for alkali metals \( \delta=\Lambda \) at T=40 K and at 300 Mc. In the temperature region around 40 K, the skin effect is anomalous or partially anomalous. The theory was developed by Reuter and Sondheimer [22] for this special case. C. Kittel extended the Dyson’s theory [23] to the anomalous skin effect. It was done assuming that the relaxation time is large compare to the diffusion time. The assumption is supported by all experiments on metals at low temperatures for which resonances were seen. The expressions for the power absorbed, and for the derivative of the power absorbed are plotted in figure 15 in the region of the 100% anomalous skin effect. Figure 16 shows the agreement between the theory and the experiment for sodium sample at T =4 K and at f =300 Mc/s.
Figure 14. Electron spin resonance in small 5 microns in diameter sodium particles. [From Ref. 21]

Figure 15(a, b, c). Electron spin resonance of lithium thick plates for different $T_D/T_2$: 0.12, 0.034 and 0.003 (for a, b and c respectively). [From Ref. 21]

Figure 16. The asymmetry parameter $A/B$ for different ratios $T_D/T_2$. [From Ref. 21]

Figure 17. The electron spin resonance absorption in the range of the completely anomalous skin effect (theory). [From Ref. 21]
2.4. Conclusions

It has been demonstrated that FMR is a powerful and useful tool for studying magnetic properties of ferromagnetic semiconductors. The analysis of the Ga$_{1-x}$Mn$_x$As sample is thought to be valid for other III$_{1-x}$Mn$_x$V alloys. The specific FMR measurements on selected samples gave the information about how the anisotropy depends on temperature, doping and strain. This is especially important, since controlling of anisotropy parameters is required for fabrication of spintronic devices and other applications. While a lot is known about resonance field, the theory of FMR’s linewidth is still poorly developed. Further efforts need to be invested into this subject which is especially complicated because of the two different broadening mechanisms. A lot is still not understood. For example, physics of in-plane anisotropy. Finally, I want to emphasize that the FMR can not be substituted in measurements of many magnetic parameters and remains very promising in the investigation of advanced structures.
Chapter 3

EXPERIMENT

The V(TCNE)$_x$ films with thickness of 4, 2 and 6 microns (for samples A, B and C respectively) were deposited on glass substrates by CVD technique at room temperature. The reaction and sample handling were performed in a glove box as described in Ref [4]. Samples were sealed in ESR-grade quartz tubes. The FMR measurements were performed on a commercial Bruker Instruments ESP300 (X-band) ESR spectrometer using a TE$_{102}$ resonant cavity. Sample temperature was varied in the range 10-300 K using an Oxford 900 continuous flow helium cryostat.

FMR absorption intensity as a function of temperature for all three samples is shown in Fig. . The temperature at which the spontaneous magnetization starts is identified as the ferromagnetic ordering temperature. FMR spectra were taken at different angles between the plane of the film and direction of the applied magnetic field. The resonance conditions for the film with a small anisotropy constant are given by the formula [9]:

$$\left(\frac{\omega}{\gamma}\right)^2 = \left[H_r + 4\pi M_{\text{eff}} \cos 2\theta\right]\left[H_r - 4\pi M_{\text{eff}} \sin^2 \theta\right]$$

(9)

where $\omega$ is the radio frequency, $\gamma$ is the gyromagnetic ratio (2.80 GHz/kOe), $\theta$ is the angle
between the plane of the film and the applied magnetic field, \( H_r \) is the applied resonance field and \( M_{\text{eff}} \) is the effective magnetization of the sample. It is assumed that the direction of magnetization \( M \) and applied field \( H \) are parallel.

For the given radio frequency \( \omega \) the parallel and perpendicular applied resonance fields are:

\[
H_{\parallel}^{\text{res}} = \left( \frac{\omega}{\gamma} \right) - 2\pi * M_{\text{eff}} \quad (10)
\]

\[
H_{\perp}^{\text{res}} = \left( \frac{\omega}{\gamma} \right) + 4\pi * M_{\text{eff}} \quad (11)
\]

This dependence of resonance field on its orientation is due to so-called demagnetization effect, which we will use to study magnetic properties of the film. From formulas (10) and (11) the value of effective magnetization is found to be:

\[
M_{\text{eff}} = \left( H_{\perp}^{\text{res}} - H_{\parallel}^{\text{res}} \right) / 6\pi \quad (12)
\]

FMR spectra for samples A, B, and C are shown on Fig. . Spectra have been recorded at different temperatures at which theirs structure is most clear. The complex structures of the spectra may be explained by “domain theory”, which implies that films
consist of regions of different domains having different magnetizations and sizes. One can see that when the angle $\theta$ is changed from $0^\circ$ to $90^\circ$ the resonance signal shifts from left to right (to the higher field region), as it is expected from Eqs. (10) and (11). A higher magnetization corresponds to a larger shift in the resonance field. The spectra of sample A have one strong peak and a few weak peaks. There are a few strong peaks in the spectra of a sample B and no complexity in the spectra of sample C. We will start the interpretation with sample B and then discuss spectra of sample A and C.

Fig. shows the integrated intensity spectrum for sample B for $\theta=90^\circ$ (the angle which allows us to get the highest resolution). The different peaks of the FMR spectrum can be assigned to different domains.

$$I = \sum_{i}^{n}\left( I_i + \frac{2 A_i}{\pi} \frac{w_i}{4(H - H_i)^2 + w_i^2} \right)$$

(13)

The volume of the domain is proportional to the area under the lorentzian peak and the value of magnetization is found using the demagnetization effect from formula (12). The peak which is on the very right of the $90^\circ$ spectrum is appeared on the very left of the $0^\circ$ spectrum and so on. The peaks just change their order when we switch the direction of the field from $90^\circ$ to $0^\circ$. The relative volumes of the domains and their magnetizations are also given in the table 1.
It is remarkable that at $\theta=30^\circ$ the spectrum is given by a single peak. This result can be predicted by analyzing formula (9). With the assumption that $H_r >> M_{\text{eff}}$, $H_r$ taken from (9) does not depend on $M_{\text{eff}}$ when $\cos^2 \theta = \sin^2 \theta$ ($\theta \sim 35^\circ$). Thus, even when there is some distribution of $M_{\text{eff}}$ there should be just one peak. On Fig. angular dependence of the resonance field for all three samples is shown. The solid curves represent the theoretical results obtained from formula (9). The experimental $M_{\text{eff}}$ for sample A gives only a 1% deviation compared to theoretical $M_{\text{eff}}$ for sample A found from formula (12). Thus, the assumptions under which formula (1) was derived are confirmed.

The small peak at the region below 3500 Oe for sample B (Fig. ) appears because of the roughness of the film. The demagnetization effect for the different roughness of the film is shifted by $90^\circ$ with respect to that of the plain film. It is also observed for sample A.

Another possible interpretation of the present FMR spectra could be exciting transverse spin waves. If we recall that the thickness of the films is of the order of 1 $\mu$m, then we can say that spin waves may be observed. The theory of standing spin-waves modes is given by the expression for the $\theta=90^\circ$ spectrum [6]:

$$\left(\frac{\omega}{\gamma}\right) = H_n - 4\pi M_{\text{eff}} + \left(\frac{2D}{M_{\text{eff}}}\right) \left(\frac{n\pi}{d}\right)^2$$

where $n$ is the number of the excited mode, $d$ is the thickness of the film and $D$ is the exchange stiffness constant. The spin-waves modes resonance fields go into the low-field direction (6), and intensity drops for higher modes as shown on Fig., which is just
opposite to the our spectra peaks behavior. Thus, the spin-wave model is not adequate for the present experiment.

Fig. demonstrates temperature dependence of $M_{eff}$, which is determined from resonance fields in parallel and perpendicular orientations. $M_{eff}$ for sample A shows long-range ordered behavior, and $M_{eff}$ for samples B and C present spin-glass behavior.

Another parameter, which was studied by FMR technique, is the linewidth. Fig. shows temperature dependence of the full width at half maximum (FWHM) at $\theta=45^\circ$ for all samples. We consider the linewidth at $\theta=45^\circ$, since the complexity of the spectra for this angle is minimal. The temperature dependence of FWHM for sample C shows behavior similar to the previously reported powder sample of V(TCNE)$_x$ with $T_c = 160$ K (doted curve) [7]. For the $T<T_c$, according to the Becker model for the spin-glasses with anisotropy, the linewidth variation is given by [15]

$$\Delta H = \frac{EFT}{F^2 + T^2}$$  \hspace{1cm} (15)

where $E=g\mu_B K/\hbar \omega \chi$ and $F=M_2/K_B \omega$, $K$ is the anisotropy constant, $M_2$ is related to spin relaxation and other symbols have their usual meanings. Parameters $E$ and $F$ for thin film C are 46 Oe and 6.8 K, and for the previously reported powder sample are 309 Oe and 5.5 K, respectively. A simple comparison of these values indicates that anisotropy in the film is smaller then in the powder sample and very small in general.
For the temperature $T \sim T_c$ (critical regime) the linewidth is given by the formula:

$$\Delta H = a_0 + b \left( \left( \frac{T}{T_{\text{min}}} \right) - 1 \right)^n$$

(16)

where $a_0$ is the residual linewidth and $T_{\text{min}}$ corresponds to the temperature for minimum linewidth. The exponent $n$, which shows the disorder of the system, does not change a lot: 2.1 compared to the previously reported 2.0. The residual linewidth is smaller for the higher $T_c$ sample because of a spin delocalization process. For the $T >> T_c$ we observe a thermal broadening regime:

$$\Delta H = (a_0 - b \theta) + bT$$

(17)

where $a_0$ is the residual linewidth, $\theta$ is the Curie-Weiss temperature and $b$ is the thermal broadening constant. For the samples A and B we can not say that the FWHM’s have the same behavior as the powder sample, because the temperature range is short, but in general we expect the FWHM drop at higher temperatures due to spin delocalization and spin diffusion, or we just say motional narrowing.
The lineshape of the samples remains almost Lorentzian in the entire temperature range. This fact is confirmed either by Lorentzian fit or by observing the ratio $\Delta H_{\text{FWHM}}/\Delta H_{\text{PP}}$, which is equal to 1.73 for Lorentzian and 1.18 for Gaussian. Based on this we conclude that the three-dimensional spin exchange interaction is presented in all samples.

The temperature dependence of integrated intensity for all three samples is shown on Fig. . The linewidth becomes narrower as the temperature approaches $T_c$, and this narrowing allows us to observe detailed structure, especially for the sample B. Another very important feature of EPR spectrum is the shift of the spectrum with temperature. The spectrum shift, which is significant for samples B and C, occurs because the films change the direction of their magnetic polarization. In other words the domains are magnetically soft at high temperatures, and directions of the magnetization are parallel to the applied magnetic field. At low temperatures the vector of magnetization is not parallel to the vector of the applied magnetic field, and because of this the spectra are shifted to the low field region. This is also consistent with the spin-glass behavior of samples B and C.

g-values for all three samples were calculated by comparing the demagnetization corrected FMR fields with a standard dpph sample’s resonance field. As depicted in Fig. , the g-values for all three samples are within the range of 1.95- 1.97. The reduction of g-values in the three samples, compared to a free electron, may not be due to a single factor, but spin-orbit coupling in $V^{2+}$ ions is likely to contribute to this. Using the second order perturbation theory
\[ g_{\text{eff}}(T) = g_0 - \Delta g e^{-\Delta E/kT} \] (18)

where \( \Delta E \) is the energy difference between the ground and first exited states. The fit for the sample C gives the result: \( g_0=1.971\pm0.001, \Delta g=2.2\times10^{-2}\pm1\times10^{-3}, \ \Delta E/k=67.52\pm6.83 \text{ K}. \) The fitting for the samples A and B is not applicable, because of the small variation of g-value.

In conclusion, we have reported a detailed analysis of the FMR data for the V[TCNE], films. FMR spectra indicate that film samples composed from magnetic domains having variation in magnitude of the effective magnetization. Such a model enables us to calculate the volumes of the domains and their effective magnetization. Temperature dependence of the integrated FMR spectra suggests that domains change the direction of their magnetic polarization. The integrated spectra of absorption have predominantly Lorentzian profiles, which means that the spin exchange interaction in the film is 3-dimensional. The angular-dependence of the resonance field for all three samples confirm the model that effective magnetization is parallel to the applied magnetic field at high temperatures.

This work was supported in part by DOE, ARO and DARPA.
Chapter 4

FMR STUDY OF FILM SAMPLES

Since its discovery by Zavoisky in 1945, electron paramagnetic resonance (EPR) has been an important method of high-resolution spectroscopy using frequencies in microwave region ($\nu \approx 10^9 - 10^{10}$ Hz). EPR technique is significantly different from ordinary microwave spectroscopy. It deals with materials whose energy levels may be varied by application of magnetic field. In other words EPR is applicable to systems with net electron spin angular momentum. These include: free radicals in the solid, liquid, or gaseous states; biradicals; systems in the triplet state; systems with three or more unpaired electrons; most transition-metal ions and rare-earth ions and some others. EPR is a sensitive technique and it yields accurate and important information unobtainable with other methods. The paper will start with the basic theory of lineshape and linewidth of EPR spectra, continue with discussion of theoretical results for polymers. At the end the experimental examples will be given. The discussion will be focused on polymer vanadium tetracyanoethylene $V[TCNE]_x$, a high-$T_c$ molecule-based magnet.

1. **Lineshape**

The EPR’s energy absorption peak is defined by formula:

$$\Delta E = h\nu = g\mu H$$  \hspace{1cm} (19)
where \( h \) is Planck’s constant, \( \nu \) is the frequency of the microwaves, \( g \) is Lande factor, \( \mu \)-Bohr magneton, \( H \) is external magnetic field. The formula (19) suggests that the absorption of energy occurs only at particular value of magnetic field. In reality absorption extends over a range of fields. EPR lines always have a finite width. The reason for this is that electrons not only respond to the external applied magnetic field, but they also interact magnetically with their environment in the sample. That is why the resultant magnetic field seen by a population of electron spins is not quite the same throughout the population. We can make the conclusion that the resonance absorption line will be obtained over a range of values centered at the resonance value given by formula (19). By studying of the line width and line shape the parameters of electron spin environment can be found. There are two equations, which are used to describe line shapes: Lorentzian and Gaussian.

\[
I = \frac{2I_0}{\pi} \frac{w}{(4(H-H_0)^2+w^2)} \quad \text{Lorentzian} \quad (20)
\]

\[
I = \frac{I_0}{w} \left( \frac{\pi}{2} \right)^{1/2} \exp \left( -2(H-H_0)^2/w^2 \right) \quad \text{Gaussian} \quad (21)
\]

where \( I_0 \) is the maximum of the intensity, \( H_0 \) is the field at maximum intensity; \( w \) is the width of the curves. In practice the observed line shapes are usually mixture of Lorentzian and Gaussian shapes. The Lorentzian shape occurs due to classical process of absorption (or emission) of radiation from harmonically bound electron. In this process
we need to interrupt the motion of the random electron immediately. In case the of EPR the described process is electron exchange. The Gaussian shape arises from the statistical distribution of neighboring spin magnetic moments with respect to the chosen. The same distribution occurs in the heights or weights of the people. The spins see different fields due to the complex environment. There is so called dipolar broadening.

![EPR Spectrum of V(TCNE), at T=300K. Magnetic Field is parallel to the film.](image)

Figure 18.
Linewidth.

The effects of the environment which result in the EPR linewidth and also affect the line-shape are referred to the relaxation times. The relaxation time is a parameter, that characterizes the reorientation of the electron spin. Let us consider the spin-lattice relaxation time, T₁ and the spin-spin relaxation time, T₂. According to the definition, the relaxation time is the time required by a system out of equilibrium to return to 1-1/e (~63%) of its equilibrium position. The process, which involves spin-lattice relaxation, that is thermal equilibration of the spin system with the lattice, is characterized by T₁. The spin-spin relaxation time T₂ is defined as a time required by system to decay from phase coherent condition (all spins are in the same direction) to the random condition. The line width and T₂ are inverse proportional:

\[
\frac{1}{T_2} = \frac{\pi g \mu_0 \Delta H_{1/2}}{\hbar}
\]  

where \(\Delta H_{1/2}\) is the line width at half of the maximum height.

The line widths have classification. An EPR line can be homogeneously broadened and inhomogeneously broadened. The homogeneously broadened line occurs in the case of spins having the same environment and inhomogeneously broadened line occurs in the case of different spins environment. But it is remarkable that the inhomogeneously broadened line consists of a large number of homogeneously broadened lines. It is possible to burn a hole in the inhomogeneously broadened line by
selective saturation of the particular homogeneously broadened line. This means that in some subpopulation the total spin of upper and lower energy states is equal to zero. This effect is shown on the Fig. . The saturation of single homogeneously broadened line is also shown. Interesting question—what is the width of homogeneously broadened line? It could be estimated from the uncertainty principle:

\[ \Delta E \Delta t = g\mu_0 \Delta H \Delta t > = \frac{h}{4\pi} \]  

(23)

where \( \Delta t \) is the lifetime of the energy (spin) state. Thus by studying of the linewidth we can find lifetime of the energy state. If we increase the microwave power the line will be broadened, since spins will spend less time in the energy levels (\( \Delta t \) will decrease), which is also shown on the Figure 19.

Figure 19.

*Dimensionality.*
The charge of the material could move in some directions, some directions are restricted. If the charge could move equally along three axes, this is the case of 3D motion, if along two axes- 2D motion, if along one axe (for example in some polymers)– 1D motion. The dimensionality of the system may be obtained from EPR spectra parameters. If we take the ratio of the intensity of the signal at resonance to the intensity of the signal off resonance and plot it against the square of the ratio of the difference between the field off resonance and resonant field and of $\Delta H_{PP}$, we can find the dimensionality of the system: that the larger the slope, the larger the dimensionality.

**EPR study of the $V(\text{TCNE})_x$**

I was doing some EPR measurements of the vanadium incorporated in tetracyanoethylene (TCNE) or simply $V[\text{TCNE}]_x$, where $x\sim 2$. The temperature-dependence and angular-dependence measurements have been done. Let us consider the theory of the temperature-dependence experiment. For these experiment the theory of linewidth and lineshape developed by K.W. Becker for the spin glasses alloys is applicable. There are three regions described by Becker model. First region is the region of temperatures higher then $T_c$. At $T>>T_c$ the linewidth behavior can be characterized in terms of thermal broadening. As it is known from the literature [Long, 1995], thermal broadening is inverse proportional to magnetization. The thermal broadening occurs due to relaxation processes in two sublattice system. According to the Curie-Weiss law, thermal broadening is directly proportional to the temperature.
\[ \Delta H = (a_0 - b\Theta) + bT , \]  

(24)

Where \( a_0 \) is the residual linewidth, \( b \) is the thermal broadening constant, and \( \Theta \) is the Curie-Weiss temperature. This behaviour is shown on the Fig. 20.

At high temperatures, it was also shown by Stewart [Stewart, 1980] that the resonance field does not depend upon temperatures.

Figure. 20

At temperatures close to \( T_C \), called critical regime, anomalous broadening occurs. The relation can describe the linewidth

\[ \Delta H = a_0 + b'\left(\frac{T - T_{\text{min}}}{T_{\text{min}}}\right)^2 , \]  

(25)
where $a_0$ is the residual linewidth, and $T_{\text{min}}$ is the temperature of minimum linewidth. The origin of residual component of linewidth is referred to crystal-field effect and local imperfections with help of demagnetization mechanism.

Huber provides another formula. It has been shown that fluctuations of the magnetization are the main source of contribution to the linewidth. For highly symmetrical systems, the linewidth is given by

$$\Delta H = A + B \xi^{3/2}.$$  \hfill (26)

As it was shown by Huber such behavior is an evidence of the high local symmetry in some regions of the sample with strong disorder between these regions.
The next regime is the region of temperatures smaller than Curie temperature. In this case the broadening of linewidth is observed as well as shift in resonance field. Decrease of the temperature causes the reduction of spin fluctuations that, in turn, reduces the effectiveness of the exchange narrowing. The linewidth and resonance field shift are given by

$$\Delta H = \frac{ABT}{B^2 + T^2} ,$$  \hspace{1cm} \text{(27)}$$

and

$$H_{\text{res}} = H_0 + \frac{AT^2}{B^2 + T^2} ,$$  \hspace{1cm} \text{(28)}$$

Where $A = g \mu_B K / h \omega \chi$, $B = M_2 / K k_B \omega$, and $H_0 = h \omega / g \mu_b$. Here $\chi$ is a static transverse susceptibility, $K$ is the anisotropy constant, and $M_2$ is related to spin relaxation.
Figure 22.
Angular dependence studies

EPR measurements were done at different angles between magnetic field and sample film. The data is shown on the Fig. 23

EPR SPECTRA FOR V(TCNE)ₓ at 298 K-DEPENDENCE ON FIELD DIRECTION

![Diagram showing EPR spectra with magnetic field and sample film orientations](image)

Figure 23
EPR Measurements

Figure 24.
Chapter 5

Conclusions

The experimental data have proven the consistence of the Becker model with respect to the V(TCNE)$_x$: above $T_c$ the linewidth (FWHM) is defined by simple broadening factor, below $T_c$ it follows $ABT/(B^2+T^2)$ law for disordered system. We also have to say that at $T>T_c$ the position of the EPR line demonstrates small angular dependence, at $T<T_c$ the line position strongly depends on the orientation of the film with respect to magnetic field due to demagnetization effect. The theory of the EPR spectra looks like the same as the theory of luminescence. The importance of the parameters such as lineshape and linewidth of the EPR spectra was could give lot information about structure of the studying materials.
APPENDIX

ADDITIONAL FIGURES AND TABLE

Fig. 1

Temperature (K)

FMR Intensity (arb. units)

Sample A $T_c > 300K$
Sample B $T_c \sim 280K$
Sample C $T_c \sim 220K$

$V(\text{TCNE})_x$ films
Fig. 2

Sample A
T = 300 K

Sample B
T = 200 K

Sample C
T = 140 K

Absorption derivative (arb. units)

H (Oe)

V(TCNE)_x

3300 3400 3500 3600 3700
Sample B
T = 200 K
T_c ~ 280 K

Absorption derivative (arb. units)

Intensity (arb. units)

Fig. 3

H (Oe)

3300 3400 3500 3600 3700

90°
Fig. 5

- **Sample A**
  - $T=300$ K
  - Experimental
  - Theoretical

- **Sample B**
  - $T=200$ K

- **Sample C**
  - $T=100$ K

Resonance Field (Gauss)

$\theta$ (°)

---

Experimental
Theoretical
Fig. 6

Sample A

$T_c > 300 \text{ K}$

Sample B

$T_c \approx 280 \text{ K}$

Sample C

$T_c \approx 220 \text{ K}$

Integrated Intensity (arb. units)

$H(\text{Oe})$

$T=20 \text{ K}$
$T=140 \text{ K}$
$T=200 \text{ K}$
$T=260 \text{ K}$
$T=300 \text{ K}$
$T=80 \text{ K}$
$T=180 \text{ K}$
Fig. 7

$V(\text{TCNE})_x$

$M_{\text{eff}}$ (Oe)

T (K)
Fig. 8

- Sample A
- Sample B
- Sample C
- Powder Sample

FWHM (Oe) vs Temperature (K)

$\theta = 45^0$
Fig. 9

$\theta = 45^0$

$V(\text{TCNE})_x$

Sample A

Sample B

Sample C

Fit

<table>
<thead>
<tr>
<th>Sample</th>
<th>$g$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.97</td>
</tr>
<tr>
<td>B</td>
<td>1.96</td>
</tr>
<tr>
<td>C</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Table 1

<table>
<thead>
<tr>
<th>Domain</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>1</td>
<td>0.35</td>
<td>0.65</td>
<td>3.17</td>
</tr>
<tr>
<td>$M_{domain}$</td>
<td>3.18</td>
<td>3.55</td>
<td>4.11</td>
<td>5.85</td>
</tr>
</tbody>
</table>


7. Z. Frait and D. Fraitova, Spin-wave resonance in metals (1988).


