Dynamic magnetic susceptibility of systems with long-range magnetic order

by

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DEDICATION

This work is dedicated to Gabe, Chi, and Jennifer.
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ABSTRACT

Results of dc magnetic field dependent measurements of the dynamic magnetic susceptibility, $\chi$, of various ferromagnetic (FM) and antiferromagnetic (AFM) materials showing a range of transition temperatures (1-800 K) are presented. Data was collected primarily with a tunnel diode resonator (TDR) at several different radio-frequencies ($\sim$10-30 MHz). In the vicinity of $T_C$, local moment ferromagnets show a very sharp, narrow peak in $\chi$ which is suppressed in amplitude and shifted to higher temperatures as the dc bias field is increased. Critical scaling analysis can be carried out on this data to determine the critical exponents, however these exponents are not extracted from the data. In contrast, itinerant ferromagnets show a broad maximum in $\chi$ well below $T_C$ which is suppressed and shifts to lower temperatures as the dc bias field is increased. The data on itinerant ferromagnets is fitted to a semi-phenomenological model that suggests the sample response is dominated by the uncompensated minority spins in the conduction band. Further effects, such as heating of magnetically ordered metallic samples due to the rf field and detection of phase transitions in the multiferroic materials Ho- and DyMnO$_3$ are also presented. The utility of the TDR as an instrument in the study of magnetically ordered materials has been expanded beyond the simple demonstration purposes. It is seen that measurements are strongly frequency dependent, however there is no simple method whereby measurement frequency can be changed in a controllable fashion. Concluding remarks suggest possible scenarios to achieve frequency resolved data using the TDR as well as other fields in which the apparatus may be exploited.
CHAPTER 1. Magnetic Measurements

1.1 Introduction

Interesting quantities to measure for magnetic samples include the magnetic moment, $M$, the magnetic susceptibility $\chi$, and the ordering wave vector $\vec{q}$. By determining these quantities and how they vary with temperature and applied magnetic field information regarding the nature of the interaction between the magnetic ions is obtained. For example, suppose a sample of some material is cooled to low temperature in zero field. A small external field is applied and the moment is measured as temperature is increased. If the magnetic moment grows and then decreases again as the temperature increases, it is likely there is a phase transition in the temperature region where the moment changes. Field cooling through the transition while measuring the moment can hint at what type of order exists. The presence or absence of magnetic hysteresis also provide clues as the magnetic structure. A feature in the magnetic susceptibility such as a peak, dip, or break in slope may provide other clues as to the nature of the magnetic order.

No single measurement will provide all the information necessary to fully characterize a sample. It is better to take a multifaceted approach and measure as many different properties as time, money, and interest permit. On rare occasions a new measurement technique is developed or an existing technique in one branch of physics is applied to a different phenomenon. In either case the data have a high probability of being novel. Such novel data are often confusing and require considerable effort to understand. The potential return is new insight into existing physical phenomena. An attempt to understand radio frequency magnetic susceptibility data from a novel measurement technique is made in this work.

This chapter begins with a basic description of the more common magnetic measurements
of magnetic moment, neutron scattering, and conventional AC susceptibility. It will proceed to a discussion of the various phenomena that may be explored with radio frequency susceptibility, placing emphasis on those phenomena that are most relevant to this work. A description of the technique used here (tunnel diode resonator) and representative data on five materials concludes the chapter.

1.2 Conventional Magnetic Measurements

Conventional measurements are defined here as those measurements performed on commercial equipment and common in the literature. There are a great many measurement techniques at the disposal of the experimentalist. However, there are three primary measurements by which practically all magnetic information is gathered. These three are measurements of DC or static magnetic moment, magnetic susceptibility, and neutron scattering. Supplementing these techniques are the slightly less common nuclear magnetic resonance (NMR), ferromagnetic resonance (FMR), electron paramagnetic resonance (EPR), Mössbauer spectroscopy, and microwave cavity perturbation. Each technique compliments the others and provides slightly different information regarding the magnetic nature of the sample under consideration.

Conventional measurements are extremely important because they offer data that are often well-understood within the confines of current theories. Interpreting these data is usually straightforward and allows for rapid and accurate comparison between different materials. When data from conventional measurements differ from those predicted by extant theories, it is an indication that some poorly understood physics might be at work.

1.2.1 DC Magnetic Moment

Measurements of the static magnetic moment of a sample are the most common methods of characterizing the magnetic properties of a material. Through static moment measurements it is possible to determine the paramagnetic moment per magnetic ion, saturation moment per ion, estimate the ordering temperature of the material, and evaluate the anisotropy in a single crystal sample. A drawback to static measurements is that a bias field is generally required.
to obtain a non–zero result. In ferromagnetic materials at temperatures below $T_C$, the bias field acts to modify the domain structure so that a bulk moment is present in the sample. For temperatures above $T_C$, the bias field opposes thermal randomization which leads to zero moment in the paramagnetic state. A remanence measurement may be done in which a large bias field is applied and then taken to zero. Subsequently, the moment is measured as a function of a different parameter. Very often the additional parameter is temperature, but it could be any other controllable parameter that may affect the magnetic moment of the sample.

1.2.2 Magnetic Susceptibility

Magnetic susceptibility measurements may be carried out in either a static or a dynamic manner. In a static susceptibility measurement a bias field is applied and the moment is measured. Then the magnitude of the moment is divided by the magnitude of the field and $\chi = M/H$ is reported. In a dynamic measurement of magnetic susceptibility, a time varying magnetic field is applied to the sample. The measured signal is obtained either through an induced voltage in a coil (conventional AC susceptometry) or a change in the natural resonant frequency of some portion of the measurement apparatus (microwave cavity perturbation and tunnel diode resonator).

Low frequency AC susceptibility measures the response of a sample to a time varying magnetic field which may be superimposed on a DC magnetic field. Unlike DC moment measurements, it is not necessary that a DC field be applied to collect the data. The measurement may be made in either a longitudinal or transverse mode. In a longitudinal measurement the AC and DC fields are coaxial, while in a transverse measurement the two fields are perpendicular. Typically the AC field is limited in frequency to less than 100 kHz. The frequency limit is caused by issues with phase noise and the difficulty associated with driving a coil far from its resonant frequency. The amplitude of the alternating field may be anywhere from 0.1-10 Oe. The fairly large drive fields are needed to provide an adequate signal to noise ratio.

Measurements of AC susceptibility have been useful in determining critical indices associated with the second order para- to ferromagnetic phase change [Ho et al. (1981), Drobac
A major drawback of these techniques is that the drive field is typically on the order of 0.1-10 Oe. Further, the driven coil method places a relatively low upper limit on the frequency that can be used to test the system.

AC susceptibility may be carried out in either an amplitude domain or frequency domain fashion. In an amplitude domain measurement the magnitude of the output signal is measured. Usually the raw output signal is a voltage. The reliability of amplitude domain measurements is limited by the waveform of the output signal. If there is significant noise or distortion in the output signal, then there will be considerable uncertainty in the AC susceptibility. Frequency domain measurements are relatively insensitive to the waveform of the output signal. Since a frequency measurement is a counting of how often a particular event occurs in a given time period, as long as there is no noise in the vicinity of the counting condition, this source of uncertainty is removed.

1.2.3 Neutron Scattering

Neutron scattering is a very powerful technique for determining the microscopic magnetic structure of a magnetic material. The wavelength of low energy neutrons is on the order of angstroms, which is the typical spacing between ions in a solid. The fairly close match between neutron wavelength and ion spacing in a crystal permits the use of a beam of neutrons as a probe of crystal structure. Neutrons are unaffected by the charge on the electrons in the lattice and primarily scatter off the nuclei. The propensity for scattering off nuclei allows a neutron to probe deep into the bulk of the sample. The neutron also has a magnetic moment, and as such it is sensitive to magnetic structure. Through neutron scattering it is often possible to determine the magnetic structure of an ordered sample from the observation of different scattering profiles above and below the ordering temperature.

1.3 Radio–Frequency Susceptibility

Many physical phenomena are observable at radio frequencies, and some of these phenomena have been explored quite extensively. Almost all of the explored rf properties are resonance
effects within the material. As such, they require frequency resolved measurements to determine a particular transition energy in the material. Useful data results from tracking how this transition energy shifts with some adjustable parameter like temperature, pressure, chemical doping, etc.

Increasing the frequency of the alternating field in AC susceptibility to 10 MHz allows for the exploration of several effects not accessible at lower frequencies. These effects include nuclear magnetic resonance, electron paramagnetic resonance, relaxation processes, domain wall resonance, as well as a probe of resistivity through the normal state skin effect. In conjunction with the normal state skin effect is the possibility of the rf field heating a metallic sample. Table 1.1 summarizes the various effects observable at radio–frequencies.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Typ. Freq. (MHz)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR</td>
<td>10-100</td>
<td>Blundell (2001)</td>
</tr>
<tr>
<td>EPR</td>
<td>≥10(^3)</td>
<td>Blundell (2001)</td>
</tr>
<tr>
<td>spin–spin relaxation</td>
<td>10(^4)</td>
<td>Morrish (2001)</td>
</tr>
<tr>
<td>spin lattice relaxation</td>
<td>10(^{-4})–1</td>
<td>Morrish (2001)</td>
</tr>
<tr>
<td>domain wall resonance</td>
<td>1–50</td>
<td>Saitoh et al. (2004)</td>
</tr>
<tr>
<td>skin effect</td>
<td>1-10(^3)</td>
<td>Jackson (1998)</td>
</tr>
</tbody>
</table>

### 1.3.1 Normal State Skin Effect

An oscillating electromagnetic field is attenuated when it penetrates a metal. The attenuation is due to the normal state skin effect. The characteristic length over which the attenuation occurs is called the skin depth and it is denoted by \(\delta\). The skin depth depends on the resistivity \(\rho\) and permability \(\mu\) of the metal, as well as on the frequency \(f\) at which the field oscillates. \(\delta\) is related to the previous three parameters by the following equation [Jackson (1998)]:

\[
\delta = \frac{c}{2\pi} \sqrt{\frac{\rho}{\mu f}}.
\]  

(1.1)
To see this, consider an oscillating electromagnetic field normally incident on a vacuum/metal interface. Maxwell’s equations for this situation may be written as

\[ \nabla \times \mathbf{B} = \frac{4\pi}{c} \mu \mathbf{J} \]  
\[ (1.2) \]

\[ \nabla \cdot \mathbf{B} = 0 \]  
\[ (1.3) \]

\[ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0 \]  
\[ (1.4) \]

\[ \mathbf{J} = \sigma \mathbf{E} \]  
\[ (1.5) \]

where \( \sigma = 1/\rho \) is the conductivity. We can replace \( \mathbf{B} \) with the vector potential by setting \( \nabla \times \mathbf{A} = \mathbf{B} \). This changes Eq. 1.4 to

\[ \nabla \times \left( \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = 0. \]  
\[ (1.6) \]

The immediate consequence of this is that

\[ \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} + \nabla \phi = 0. \]  
\[ (1.7) \]

Provided there are no free charges, it is appropriate to set \( \phi = 0 \), whence \( \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \). Further, by combining Eqs. 1.2, 1.5, and 1.7, and by exploiting the vector identity \( \nabla \times \nabla \times \mathbf{A} = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} \) we arrive at

\[ \nabla^2 \mathbf{A} = \frac{4\pi}{c^2 \mu \sigma} \frac{\partial \mathbf{A}}{\partial t}. \]  
\[ (1.8) \]

If a plane wave magnetic field of the form \( H_x(t) = H_0 \cos 2\pi ft \) is normally incident (in the \( z \) direction) on the metal in question, continuity conditions require the parallel component of \( H \) be conserved on crossing the boundary between the vacuum and the metal. Further, Eq. 1.8 requires that the magnetic wave in the medium have only an \( x \) component and travel in the \( z \). Provided the conductivity is constant in space, \( \mathbf{B} \) (as well as \( \mathbf{H} \)) will have the behavior
of \( A \) in Eq. 1.8. Therefore, in the medium it is expected that

\[
H_x(z, t) = h(z) e^{i\omega t}
\]  
(1.9)

and

\[
\left( \frac{d^2}{dz^2} - \frac{4\pi i\mu \sigma \omega}{c^2} \right) h(z) = 0.
\]  
(1.10)

This problem has a common form with an expected solution \( h(z) = h_0 e^{kz} \). Substituting this gives the condition

\[
k = \pm (1 + i) \frac{2\pi}{c} \sqrt{\mu \sigma f}.
\]  
(1.11)

In the above \( f = \omega / 2\pi \) is the frequency of the oscillating wave as measured in hertz rather than radians per second. \( k \) has the dimensions of inverse length and characterizes the decay of \( h \) in the medium. Consequently, we define \( \delta = 1/k \), arriving at the skin depth of the metal as given in Eq. 1.1. Figure 1.1 is a cartoon representing the decay of the magnetic field in the metal. From here we can proceed to the calculation of the AC susceptibility of a metal.

Within the metal, we can write the vector potential of the decaying field as

\[
A = -B \frac{\delta \sinh (2x/\delta)}{2 \cosh (2R/\delta)} \hat{z}
\]  
(1.12)

Equation 1.2 allows for a relation between \( A \) and \( J \), after exploiting the previously mentioned vector identity.

\[
\nabla^2 A = \frac{4\pi}{c} J
\]  
(1.13)

This gives the current density in the metal as a function of position, or depth, as

\[
J = B \frac{c}{4\pi \delta \cosh (2R/\delta)} \frac{2 \sinh (2x/\delta)}{\delta} \hat{z}
\]  
(1.14)

The magnetic moment induced in the sample can be determined from

\[
M = -\frac{1}{2c} \int r \times J d^3r
\]  
(1.15)
Figure 1.1 Cartoon of decay of an oscillating magnetic field in a metal.
Evaluating this over the limits 0 to R gives the following expression for the moment.

$$4\pi M = \left( \frac{B\delta}{2R} \tanh \frac{2R}{\delta} - H \right) \hat{y}$$

(1.16)

Differentiating once with respect to $H$ gives the susceptibility from the sample as

$$4\pi \chi = \frac{\mu \delta}{2R} \tanh \frac{2R}{\delta} - 1$$

(1.17)

From Eq 1.17 we can extract some information that will be useful in analyzing the data. First, in magnetically static samples with permeability $\mu = 1$ the radio–frequency susceptibility will track the resistivity. This is demonstrated for copper in Fig. 1.5 where it is seen that the low temperature resistivity follows a $T^2$ behavior as expected for a simple metal [Ashcroft and Mermin (1976)]. This also applies to field or magneto-crystalline anisotropy saturated magnetic samples wherein the ac-susceptibility of the spins is essentially zero. That this is so is evident from Fig. 4.6 where the unusual $T^{5/3}$ behavior of $\rho$ at low temperatures in ZrZn$_2$ is recovered. This fact has been exploited in the past to probe the Fermi surfaces of metals [Coffey et al. (2000), Prozorov et al. (2006)] via the Shubnikov-de Haas effect [Shoenberg (1984)]. In magnetically active samples, however, the situation is less clear due to the mixing of the magnetic permeability and resistivity through the product $\mu \delta$. There are two limiting cases. First, in the limit $2R << \delta$, the hyperbolic tangent goes to zero linearly and the susceptibility reduces to $4\pi \chi = \mu - 1$, which is the standard relation, valid when the magnetization in a sample is uniform. This is the insulating regime, and the resonator probes the response of the magnetic moments in the sample. In the other limit ($2R >> \delta$), the hyperbolic tangent term is very close to 1 and $4\pi \chi = (\mu \delta/2R) - 1$. This is a complicated case because there is a mixing of the permeability and the resistivity. Further, substitution of $1 + 4\pi \chi$ for $\mu$ is not valid as such a substitution requires the magnetization to be uniform in the sample. This clearly is not the case since the applied field decays exponentially in the sample. This represents the skin depth limited regime, and here it can be argued that the resonator probes the changes in resistivity concomitantly with changes in the magnetic permeability. For ferromagnets that are far from
the insulating regime, information regarding the response of the magnetic moments can be obtained provided the temperature is close to $T_C$. In this temperature range the susceptibility grows rapidly, formally diverging at $T_C$. Further, $\rho$ remains finite. This implies the skin depth goes very small and the hyperbolic tangent term saturates to 1. In this case

$$4\pi \chi = \frac{c}{4\pi R} \sqrt{\frac{\rho}{\mu}} \sqrt{\mu - 1}. \quad (1.18)$$

This is seen by recognizing that the numerator of the coefficient on the hyperbolic tangent term is $\mu \delta$. Since $\delta \sim \sqrt{\mu - 1}$ the product $\mu \delta \sim \sqrt{\mu}$.

### 1.3.2 Energy Scales Associated With RF Fields

Any magnetic field (static or oscillating) gives rise to a Zeeman splitting in the energy levels of any magnetic moment. The amplitude of the Zeeman splitting is given by

$$U_{Zeeman} = \vec{m} u \cdot \vec{H}. \quad (1.19)$$

where $\vec{m} u$ is the magnetic moment and $\vec{H}$ is the magnetic field. If $\mu$ is equal to one Bohr magneton and $H$ is one tesla then $\mu H \approx 5.79 \times 10^{-5}$ eV. Comparing this to thermal energy ($k_B T$) gives an equivalent temperature of about 0.67 K. For small magnetic fields, on the order of 0.25 T or less, at temperatures above 2 K, the Zeeman energy is not expected to have a considerable effect.

In addition to the possibility of a Zeeman energy, an oscillating electromagnetic field has an energy associated with the frequency of oscillation. This is the energy of the photon associated with the wave. For a wave with a frequency of 10 MHz, the energy is on the order of $10^{-8}$ eV. Comparing the photon energy to thermal energy results in an equivalent temperature of approximately $10^{-3}$ K.

There is power dissipated in a metallic sample due to the screening from the normal skin effect. An estimate of the order of magnitude of this power can be made by considering the
energy density of the screened rf field. This is given by

\[ \varepsilon = \frac{B_{rf}^2}{8\pi}. \]

Without knowledge of the magnitude of the screened field, it is impossible to determine the energy density associated with the screening. However, the rf field used to measure \( \chi \) in this work has a peak amplitude of about 5 mOe. This magnetic field has an energy density on the order of 1.5 pJ/cm\(^3\). For the working frequencies \((10^7 \text{ Hz})\) and typical sample sizes \((1 \text{ mm}^3 = 10^{-9} \text{ cm}^3)\) here, the power dissipation is on the order of 0.01 pW in a magnetically dead sample. If there is significant magnetic permeability in the sample, this power can increase (Ch. 6) provided the heat capacity of the sample is low enough.

### 1.4 The Tunnel Diode Resonator

In order to measure the magnetic susceptibility at 10’s of MHz at tunnel diode resonator (TDR) was employed. The TDR is a self-resonating \( LC \) circuit driven by a tunnel diode (TD). The TD is a solid state diode with a heavily doped p-type terminal. The \( pn \) junction is of the order of 100 \( \AA \), very narrow for a diode [Esaki (1976)]. The resulting device exhibits negative differential resistance when biased within a certain range of voltages (Fig. 1.2). When biased to this region, the TD can perform as a low current, alternating current power source. If we consider a simple \( LC \) tank circuit the frequency of the ac power delivered by the tunnel diode is determined by the frequency of the tank circuit. Indeed, it is this frequency matching that is exploited in the use of a TDR. The main advantage of making measurements this way is that inductance is placed on equal footing with capacitance. Commercial capacitance bridges are capable of attofarad resolution. However, determining small changes in inductance is not simple with commercial devices. By changing the measurement from a balance of inductances to a direct measurement of resonant frequency, the sensitivity to changes in \( L \), and hence \( \chi \), is greatly improved. Further, the amplitude of the probe field is extremely small. The biasing of the TD creates a small static field in the probe coil on the order of 30 mOe in the
resonators used here. Superimposed on this is a small ac ripple that is used as the probe field, the amplitude of which is determined by the excursions up and down the $I - V$ curve. The deviations in current from the bias point are estimated to be $\leq 5 \mu$A. The resulting ac field is then $\leq 6$ mOe peak to peak. This is 1.5 orders of magnitude smaller than the typical excitation fields used in conventional low frequency ac-susceptibility.

Figure 1.2 $I-V$ curve for BD3 tunnel diode. Negative differential resistance is evident for bias voltages between 50 and 250 mV. Optimal biasing is for this particular diode is about 60-100 mV.

The TDR was developed in the 1970’s. Many different groups constructed these devices and suggested measurements including NMR spectroscopy [Aslam and Weyhmann (1973)] and magnetic susceptibility [Clover and Wolf (1970), Habbal et al. (1975), Fox and Trefay (1975)]. The main development of the TDR as an ultraprecise scientific instrument was carried out by VanDegrift in the middle 1970’s [VanDegrift (1975a)]. The primary use of the TDR in that work was in measuring dielectric constants. VanDegrift demonstrated that part per billion sensitivity could be achieved through careful design. To date, the apparatus has not been employed by many research programs. Those programs that do employ some version of the TDR are largely
concerned with precise measurements of temperature dependent magnetic penetration depth in various superconductors. A few other groups are concerned with measuring normal state magnetic effects, however their work is largely confined to thin films and nanoparticles. In the course of this work, the TDR has been employed to measure many different types of compounds and effects including ferromagnetic and antiferromagnetic conductors and insulators [Vannette et al. (2008d)], charge ordering effects in Ba$_2$NaOsO$_6$, spin glass behavior in LiV$_2$O$_4$ [Zong et al. (2008)], ferroelectric transitions, quantum oscillations in metals [Prozorov et al. (2006)], and the penetration depth in a host of superconductors (see Table 1.2). The main thrust of this work, though, was the study of the differential magnetic susceptibility ($\chi = \partial M/\partial H$) of magnetically ordered samples as functions of temperature and field in an attempt to extract information regarding phase changes and the different responses of local and non-local ferromagnets.

The versatility of the TDR is evident from the material phase space that can be explored. Table 1.2 lists the samples measured in the course of this work. Most are unrelated to this dissertation, however the list is meant to demonstrate the breadth of application of the technique.

![Figure 1.3 Schematic of the basic tunnel diode resonator circuit.](image)

The basic tunnel diode resonator circuit is shown in Fig. 1.3. The primary inductor and capacitor are $LP$ and $CP$ respectively. The sample is placed in the bore of $LP$. Inductor $LT$ is the tap coil, and it serves to shunt some of the power supplied by the diode to ground, thereby permitting extremely weak resonance. The weaker the resonance is, the fewer harmonics are present. Too many higher harmonics distort the waveform. If the harmonics are particularly
strong, the wave distortion can be significant enough to lead to miscounts in the frequency measurement. The purpose of $C_1$ and $C_2$ are to decouple the tank circuit from the rest of the electronics. $C_1$ is typically on the order of 50 pF while $C_2$ is on the order of 10 nF. At 10 MHz the rf impedance of $C_1$ and $C_2$ are 340 $\Omega$ and 1.5 $\Omega$. Thus, $C_2$ is practically a short to ground for the rf signal and only a very small portion is passed back up the line by $C_1$. $R_1$ and $R_2$ act as voltage dividers. $R_3$ is termed the parasite resistor. It acts in concert with the tap coil to reduce unwanted oscillations. $R_1$ has a typical value of 1.4 k$\Omega$, $R_2$ and $R_3$ are 300 $\Omega$. The primary coil is wound of 40 AWG enameled copper wire. It is on the order of 60 turns with one wire diameter space between each turn. This allows the coil to more closely approximate a pure inductance by limiting the stray capacity from adjoining turns. Primary coils are wound on a former (usually the chuck end of a drill bit) lightly coated with grease and wrapped in polyester film. Once the coil is made, it is encased in Stycast 1266 epoxy (or similar) and after curing, is removed from the former. The polyester film is removed from the inside wall of the coil, and ideally the primary is just a coil of copper magnet wire suspended by an epoxy film. The tap coil is wound in a similar manner as the primary. The main difference being that the tap is left on a fused silica tube of the same outer diameter as the primary coil former. Also, the tap coil is not set in epoxy. Rather varnish is used to keep the turns of the tap glued to the tube. This allows for easy modification of the tap coil inductance. The ratio of $LP:LT$ is about 3:1. For optimal performance this ratio must be tuned experimentally for each circuit by overtapping the circuit (i. e. intentionally making the tap coil too large) and then through successive cool downs, gradually unwinding the tap until the circuit spontaneously resonates only below about 40 K. TDR’s will operate at room temperature, but the sensitivity drops from 0.001 ppm to about 1-10 ppm. This latter sensitivity is still quite good, but by operating at low temperatures with marginal oscillations, the greater sensitivity is achieved. The value of $CP$ is chosen to keep the resonance less than 50 MHz. This range was chosen because amplifiers and filters that operate well at these frequencies may be easily acquired. Further, keeping the frequency below gigahertz limits problems associated with transmission line and connector size effects that may occur when the wavelength of the radiation approaches
the typical dimensions these components. In principle, the TDR can be made to operate at higher frequencies, even into the GHz regime. This was not attempted here, but is a direction of future work (see Ch. 7). Thermal cycling of the circuit is expected to alter the resonant frequency of the circuit. The expansion and contraction of the coil, wires, solder joints, and commercial components all contribute to this effect. Fig. 1.4 plots the empty coil resonant frequency of the $^4$He for nine consecutive runs over the course of two months. The uncertainty in the recorded empty coil resonance is on the order of 0.5 Hz for the system used here. The resonance stays constant to within about 0.5% ($\pm 50$ kHz on 28 MHz) in this time period. Between the first run shown and the unshown zeroth run the coil had to be removed to recover a sample that had dropped off the sample holder. The empty coil resonance of this zeroth run was 27.76 MHz. Having to resolder these joints resulted in a change in the resonance on the order of 2%. This suggests that provided no modifications to the circuit are made, including fixing poor solder joints, the resonant frequency is very robust to thermal cycling.

![Figure 1.4](image_url)  
**Figure 1.4** Empty coil resonance vs. thermal cycle count.
Table 1.2  Samples run in TDR during this project. $T_{\text{char.}}$ is a characteristic temperature for the sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{char.}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferromagnets</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeAgSb$_2$</td>
<td>9.8 K</td>
<td>Prozorov et al. (2006)</td>
</tr>
<tr>
<td>GdPtIn</td>
<td>68 K</td>
<td>Vannette et al. (2008a)</td>
</tr>
<tr>
<td>CeVSb$_3$</td>
<td>4.5 K</td>
<td>Vannette et al. (2008d)</td>
</tr>
<tr>
<td>YTiO$_3$</td>
<td>27 K</td>
<td></td>
</tr>
<tr>
<td>EuS</td>
<td>16 K</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>280 K</td>
<td></td>
</tr>
<tr>
<td>ZrZn$_2$</td>
<td>28 K</td>
<td>Vannette and Prozorov (2008)</td>
</tr>
<tr>
<td>Ni</td>
<td>760 K</td>
<td></td>
</tr>
<tr>
<td>GdFe$<em>2$Zn$</em>{20}$ &amp; dopings</td>
<td>$\leq$86 K</td>
<td>Vannette et al. (2008d)</td>
</tr>
<tr>
<td>Fe$_{1/4}$TaS$_2$</td>
<td>160 K</td>
<td>Vannette et al. (2008c)</td>
</tr>
<tr>
<td>NiMnSb</td>
<td>730 K</td>
<td></td>
</tr>
<tr>
<td><strong>Antiferromagnets</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SmAgSb$_2$</td>
<td>10 K</td>
<td>Prozorov et al. (2006)</td>
</tr>
<tr>
<td>MnSi</td>
<td>35 K</td>
<td></td>
</tr>
<tr>
<td>FeGe</td>
<td>279 K</td>
<td></td>
</tr>
<tr>
<td><strong>Multiple Transitions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeSb</td>
<td>many</td>
<td>Vannette et al. (2008d)</td>
</tr>
<tr>
<td>Ce$<em>3$Al$</em>{11}$</td>
<td>6 &amp; 3.8 K</td>
<td>Vannette et al. (2008d)</td>
</tr>
<tr>
<td>Y$_9$Co$_7$</td>
<td>6.7 K &amp; 2.9 K</td>
<td>Gordon et al. (2008b)</td>
</tr>
<tr>
<td><strong>Superconductors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgB$_2$</td>
<td>38 K</td>
<td>Martin et al. (2008)</td>
</tr>
<tr>
<td>Re$_3$W</td>
<td>7.4 K</td>
<td>Zuev et al. (2007)</td>
</tr>
<tr>
<td>YNi$_2$B$_2$C</td>
<td>16 K</td>
<td>Prozorov et al. (2007)</td>
</tr>
<tr>
<td>ErNi$_2$B$_2$C</td>
<td>12 K &amp; 6 K</td>
<td>Prozorov et al. (2008a)</td>
</tr>
<tr>
<td>ErRh$_4$B$_4$</td>
<td>10 K &amp; 1.9 K</td>
<td>Prozorov et al. (2008b)</td>
</tr>
<tr>
<td>TmNi$_2$B$_2$C</td>
<td>10.2 K &amp; 1.8 K</td>
<td>Prozorov et al. (2008a)</td>
</tr>
<tr>
<td>Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$</td>
<td>22 K</td>
<td>Gordon et al. (2008a)</td>
</tr>
<tr>
<td>Bi-2201</td>
<td>35 K</td>
<td></td>
</tr>
<tr>
<td>OsB$_2$</td>
<td>2.1 K</td>
<td>Singh et al. (2007)</td>
</tr>
<tr>
<td><strong>Other Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiV$_2$O$_4$</td>
<td>2 K</td>
<td>Zong et al. (2008)</td>
</tr>
<tr>
<td>Ba$_2$NaOsO$_6$</td>
<td>6 K</td>
<td></td>
</tr>
<tr>
<td>HoMnO$_3$</td>
<td>many</td>
<td>Vannette et al. (2008b)</td>
</tr>
<tr>
<td>DyMnO$_3$</td>
<td>many</td>
<td>Vannette et al. (2008b)</td>
</tr>
<tr>
<td>“Fe$_8$”</td>
<td>none</td>
<td>Engelhardt et al. (2007)</td>
</tr>
<tr>
<td>Mo$<em>{72}$Fe$</em>{30}$</td>
<td>1 K</td>
<td>Schroder et al. (2008)</td>
</tr>
<tr>
<td>Mo$<em>{72}$Cr$</em>{30}$</td>
<td>none</td>
<td>Schroder et al. (2008)</td>
</tr>
<tr>
<td>CaFe$_2$As$_2$</td>
<td>170 K</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>
1.5 Measuring Changes in Magnetic Susceptibility

In exploiting a TDR the measurement of magnetic susceptibility is shifted from the amplitude domain to the frequency domain. As has been stated previously, amplitude domain measurements depend on the actual amplitude of the signal and, in AC measurements, the shape of the signal waveform. Frequency domain measurements are only concerned with counting how many times something happens in a given period. As such, frequency measurements are quite easy to do with very high precision. Since the TDR is a device that is locked onto the resonant frequency of the $LC$ tank circuit, changes of the resonance can be linked directly to either the inductor (as is done here) or the capacitor. Careful design and good thermal stability can result in a circuit that resonates in the megahertz band with a stability of 0.05 Hz over hours to days. If field or temperature is varied, the resonant frequency shifts due to the changing properties of the sample. It is this shift in resonance that is measured to determine the dependencies of $\chi$ on these two parameters.

The frequency of oscillation for an inductor-capacitor circuit with inductance $L$ and capacitance $C$ is given by

$$f_0 = \frac{1}{2\pi\sqrt{LC}}$$

(1.21)

If the inductance changes a small amount to $L + \Delta L$ the new frequency can be written as

$$f_0 + \Delta f = \frac{1}{2\pi\sqrt{(L + \Delta L)C}}$$

(1.22)

Expanding this expression for small values of $\Delta L$ and canceling gives

$$\Delta f \approx -\frac{1}{2} \frac{\Delta L}{L} f_0$$

(1.23)

From the definition of self inductance

$$L = \frac{d\Phi}{dI}$$

(1.24)

where $\Phi$ is the integrated magnetic flux in the coil and $I$ is the current producing the flux. For
an empty coil

\[ \Phi = B_0 V_c \]  \hspace{1cm} (1.25)

Here, \( V_c \) is the coil volume. In cgs units, the flux density \( B_0 \) is equal to the magnetic field \( H_0 \) in vacuum. Introducing a sample with zero demagnetization changes the flux density in the volume of the sample. This is accounted for by imagining the sample replaces the initial flux with a new value given by \( \Phi' \) where

\[ \Phi \rightarrow \Phi' = B_0 V_c + (B_s - B_0)V_s. \]  \hspace{1cm} (1.26)

The flux density in the sample, \( B_s \), is given by the usual relation

\[ B_s = H_0 + 4\pi M_s \]  \hspace{1cm} (1.27)

where \( M_s \) is the sample magnetization per unit volume. Substituting this results in the following expression for flux in the inductor:

\[ \Phi' = H_0 V_c + 4\pi M_s V_s \]  \hspace{1cm} (1.28)

Writing the derivative of \( \Phi' \) with respect to current as

\[ \frac{d\Phi'}{dI} = \frac{d\Phi'}{dH} \frac{dH}{dI} \]  \hspace{1cm} (1.29)

allows the new inductance to be written as

\[ L' = (V_c + 4\pi V_s \chi) \frac{dH}{dI} \]  \hspace{1cm} (1.30)

The first term is the empty coil inductance and the second is the change caused by the sample. Returning to equation 1.23,

\[ \frac{\Delta f}{f_0} \approx -\frac{1}{2} \frac{V_s}{V_c} 4\pi \chi \]  \hspace{1cm} (1.31)
The above expression relates the measured change in frequency to the real part of the ac-susceptibility of the sample. Equation 1.31 shows that the change in frequency, $\Delta f$, is proportional to the base frequency, $f_0$. This means a larger signal is expected with higher base frequencies, all other things being equal. If there is non-zero demagnetization for the sample the true susceptibility ($\chi_t$) may be written as

$$\chi_t = \frac{\chi_m}{1 + 4\pi N \chi_m}.$$  

(1.32)

$\chi_m$ is the measured susceptibility as related to the measured frequency shift given above.

Thus, the change in resonant frequency is directly proportional to the dynamic magnetic susceptibility of any sample placed in the coil. An increase in magnetic susceptibility results in a decrease in resonant frequency and vice versa.

It is worth noting that this technique is not well suited to measuring the absolute value of $\chi$ in most samples. The main use is to measure changes in the properties relative to some arbitrarily chosen reference value. Thus, this technique is good for determining the general dependencies of $\rho$ and $\chi$ on temperature and field. It is possible to determine the absolute value of the measured $\chi$, but this is an extrinsic property of the particular sample. Care must be taken when comparing the results of such measurements across different samples to choose samples that are of similar size and shape. Maintaining a consistent geometry across different samples maintains a consistent coefficient linking frequency shifts to susceptibility. This permits a more accurate comparison between samples of different compositions.

In practice one measures the difference, $df$, between the circuit frequency, $f_{res}$ and a local oscillator, $f_{LO}$ ($df = f_{LO} - f_{res}$). The local oscillator frequency is set higher than the circuit resonance ($f_{LO} > f_{res}$). In this way an increasing susceptibility is marked by an increasing $df$. Further, an increasing resistivity results in an increasing $df$ since the skin depth increases with the resistivity resulting in decreased diamagnetic screening.
1.6 Representative TDR Data

In this section data on various systems are presented. The measured susceptibility of a copper block is shown and straightforward analysis based on Eq. 1.17 demonstrates that variations in resistivity with temperature dominate the response of the the TDR. Next data on a triplet of rare-earth transition metal compounds (\( R\text{AgSb}_2, R = Y, \text{Ce, Sm} \)) are presented. These compounds were chosen based on their magnetic ordering properties. \( \text{YAgSb}_2 \) is non-magnetic and consequently manifests no order. \( \text{CeAgSb}_2 \) manifests a canted antiferromagnetic order at 9.8 K. The canting of the Ce moments gives rise to a net magnetic moment, so it shows ferromagnetic order along a particular crystallographic axis. \( \text{SmAgSb}_2 \) manifests pure antiferromagnetic order at approximately 10 K. Data from these three related systems form a baseline to which other compounds will be compared. Finally data on CeSb are presented. CeSb manifests a multitude of magnetic phases when the applied magnetic field and temperature are varied. It will be shown that the TDR is capable of detecting the majority of these phase boundaries.

1.6.1 Copper

Copper is a 3d metal with a filled valence electron shell. As such, it is a non-magnetic material. The absence of magnetic moments allows for a test of the resistivity contribution to the rf susceptibility. In a normal metal the thermal variation in the low temperature resistivity is dominated by electron-electron scattering. The variation in resistivity due to the mutual electron scattering is quadratic in temperature Ashcroft and Mermin (1976). In an imperfect metal there is also a residual resistivity term coming from lattice imperfections. The residual resistivity is constant.

In order to test the rf response of a simple metal, a rectangular block \((1.5 \times 0.5 \times 0.5 \text{ mm}^3)\) of copper was cut from a copper plate using metal shears. The resulting block was washed in concentrated nitric acid and rinsed in distilled water three times in an attempt to remove any magnetic shavings from the shears. The sample was mounted on a saphire rod with low temperature grease and placed in the coil of a TDR. The change in resonant frequency was
recorded as temperature was varied. The measured susceptibility was converted to resistivity through Eq. 1.17. The resulting inferred resistivity was plotted against $T^2$ as shown in Fig. 1.5. The inferred resistivity, in arbitrary units, closely follows a quadratic temperature variation from $x$ to $y$ K. At the low end the resistivity is dominated by the residual resistivity. As the temperature grows, lattice vibrations (phonons) begin to contribute significantly and the resistivity deviates from purely quadratic. This experiment demonstrates that in the absence of magnetic moments the rf susceptibility of a metal as measured by the TDR is dominated by the resistivity. This means that the measured susceptibility is an extrinsic property which depends on sample size and shape.

1.6.2 $R\text{AgSb}_2$

Myers et al. (1999b) studied the tetragonal $R\text{AgSb}_2$ family of compounds. These compounds manifest a variety of magnetically ordered states. In particular, CeAgSb$_2$ shows a
canted antiferromagnetism lying in the ab plane at approximately 9.8 K. The canting of the antiferromagnetic moments manifests itself as a ferromagnetic component along the c axis. SmAgSb₂ undergoes a transition to simple antiferromagnetic order at approximately 10 K. The non–magnetic YAgSb₂ allows for a study of how the presence of magnetic moments and/or magnetic order affect properties like resistivity and heat capacity. One sample of each of these three compounds was studied in the TDR to observe how the rf susceptibility differs across the three magnetic flavors (ferromagnetism, antiferromagnetism, and non–magnetic).

Figure ?? compares scaled susceptibility of Y–, Ce–, and SmAgSb₂ vs. temperature in the range 3–15 K as measured in the TDR. All three data sets are shifted so that the low temperature data overlap. YAgSb₂ shows a monotonic behavior through the entire temperature regime. The yttrium data appears noisy compared to the other two data sets. In fact, all data sets have approximately the same level of noise. Due to the small variation in the measured susceptibility, the yttrium data had to be magnified by a factor of approximately 100 so that the variation in \( \chi \) with temperature could be discerned. SmAgSb₂ also manifests monotonic behavior through the entire temperature range. However, at approximately 9 K there is a sharp break in the slope of the \( \chi \) vs. \( T \) graph. This temperature corresponds to the Nèel temperature, below which antiferromagnetic order sets in. In a magnetically ordered state conduction electrons can no longer scatter off ionic moments. The loss of this scattering mechanism generally leads to a decrease in the measured resistivity. Contrary to the other two compounds, CeAgSb₂ manifests non–monotonic behavior over the reported temperature range. At approximately 9.8 K a sharp peak in \( \chi \) is observed. The peak in \( \chi \) is associated with the increase in spin susceptibility due to strong ferromagnetic correlations. Below the ordering temperature the cerium compound exhibits a decrease in the measured susceptibility due to the loss of spin disorder scattering.

Static moment measurements of antiferromagnetic compounds show that the moment increases as the Néel temperature is approached. This is often reported as an increase in the susceptibility of the compound. Similar increase in moment is observed in ferromagnetic materials as the Curie temperature is approached. However, the TDR data shows that the two
different magnetic orders show different rf susceptibilities. The observed difference can be qualitatively understood based on the following argument. The perturbation field from the TDR coil is very small, being less than 5 mOe. The existence of magnetic order at a finite temperature implies an interaction between the moments in the sample. The strength of that interaction must be on the order of the thermal energy present at the ordering temperature. The perturbing field causes a change in the direction of a particular moment, tending to align the moment with the field. Near an ordering temperature the internal interactions between the perturbed moment and its neighbors dominates the response of the system. When the interaction is ferromagnetic neighboring moments have an energy advantage if they align with the perturbing field as well. This sets up a positive feedback, and the TDR sees a dramatic increase in the susceptibility of the material. Conversely, if the interaction is antiferromagnetic individual moments will tend to align so that there is no bulk magnetization in the sample. The TDR then sees no increase in $\chi$, and the response through the transition is to follow the resistivity.

The differing measured susceptibilities across the three rare–earth silver diantimonides are taken as standards to which other results may be compared. Comparison with these standards will offer an initial interpretation of a given set of data. A sharp peak in $\chi$ at a particular temperature is associated with the onset of ferromagnetic order. A dramatic drop in $\chi$ at a particular temperature is associated with antiferromagnetic ordering in a metallic sample. Temperature dependent $\chi$ that manifests no obvious features will be taken to mean the sample shows no magnetic order.

### 1.6.3 Multiple Magnetic Phases in CeSb

As an example of the utility and sensitivity of the TDR the $H - T$ phase diagram of CeSb was determined solely from measurements of $\chi_{ac}$ using the $^3$He. CeSb has been well studied and is known to manifest a complex magnetic phase diagram. It forms a layered structure with magnetic ordering occurring in some of the layers while others remain paramagnetic as determined via heat capacity [Roussat-Mignod et al. (1980)] and neutron diffraction [Lebech
et al. (1980)].

Figure 2.9 shows a temperature scan for the compound CeSb in zero applied field. This compound is well known to have multiple magnetically ordered phases in field-temperature space [Wiener and Canfield (2000)]. The TDR reproduces the phase diagram presented therein (see Fig. 2.10) as well as those reported previously [Bartholin et al. (1975), Meier et al. (1978), Roussat-Mignod et al. (1980), Escorne et al. (1981)]. Each transition into a new phase results in a kink in the measured susceptibility. This kink may originate in either the resistive or spin contributions to susceptibility. Either way, the transition would be observed.

![Temperature scan for CeSb in zero applied field](image)

Figure 1.6  

Plot of difference between TDR resonant frequency, \( f_{\text{res}} \), and a fixed local oscillator, \( f_{\text{LO}} \) versus temperature in zero applied magnetic field. This difference is proportional to \( \chi \). As described in the text, \( f_{\text{LO}} > f_{\text{res}} \). Inset shows the derivative of the main plot. The small peak near 3 K in the derivative plot is from the superconducting transition of a small amount of tin flux left from the crystal growth.

The phase diagram developed by the TDR was generated by measuring \( \chi \) parallel to the c axis of the sample. This means the resistivity in the ab plane was probed. Further, only temperature sweeps were performed in constant magnetic field. These facts taken in tandem
can account for the missed lines in the TDR data, however it does not account for the observed lines not seen in other data. The general nature of this difference was not explored, rather the measurement was performed as a check on the capabilities of the TDR. The strong similarities between the published and measured phase diagram clearly demonstrate that this apparatus can be applied to more systems than just superconductors.

Figure 1.7 Phase diagram for single crystal CeSb. Hollow points are from Wiener and Canfield (2000) while solid points are TDR data.

1.7 Summary

Radio–frequency susceptibility measurements provide data not accessible through other means. The convolution of resistivity and magnetic spin responses in metals complicates the measurement process. It is possible to circumvent these problems through careful choice of samples. The tunnel diode resonator is a method whereby extremely precise rf $\chi$ data may be collected. It was shown that there are stark differences between ferromagnetic, antiferromagnetic, and non–magnetic metals. In addition the TDR has proven sensitive to multiple phase
changes in a single material. In the following chapters an attempt will be made to understand the differences in the measured $\chi$ of various samples.
CHAPTER 2. Local Moment Ferromagnets

2.1 Introduction

In this chapter the nature of local moment ferromagnets is explored. These are systems wherein the magnetic moment is strongly localized around a particular ion or particular ions in the crystal. Typically the 4f rare earth systems are considered local moment systems as the f electrons responsible for the atomic magnetic moment are buried deep in the core of the electron cloud. Local moment magnetic systems can be either metals or insulators, however the latter are fairly rare.

2.2 Basics of Magnetism

Experimentally, it is known that the magnetic susceptibility, \( \chi = \partial M / \partial H \), of a collection of non-interacting spins varies inversely with the temperature \( T \) of the system.

\[
\chi = \frac{C}{T} \tag{2.1}
\]

\( C \) is called the Curie constant and its magnitude depends on the strength and number of the individual moments in the system.

The genesis of this dependency is in the Zeeman energy for a free spin in a magnetic field, \( U_Z = -\mu_B \mathbf{H} \cdot (\mathbf{L} + g_0 \mathbf{S}) \) where \( \mu_B = e\hbar/2m_e c \) is the Bohr magneton and \( g_0 = 2(1 + \alpha/2\pi + O(\alpha^2) + ...) \approx 2 \) is the electronic g-factor. \( \alpha \) is the fine structure constant, given by \( e^2/\hbar c \approx 1/137 \). Due to the small size of \( \mu_B \) (\( \approx 5.8 \times 10^{-4} \) ev/T), this energy is usually small compared to all other energies under consideration. The problem may then be handled using perturbation theory. If the exact eigenstates for the system in the absence of the magnetic field
are known, second-order perturbation theory may be used to determine the change in energy due to the magnetic field [Ashcroft and Mermin (1976)].

\[
\Delta U_n(H) = \mu_B \mathbf{H} \cdot < n | \mathbf{L} + g_0 \mathbf{S} | n > + \mu_B^2 \sum_{n \neq n'} \frac{| < n | \mathbf{H} \cdot (\mathbf{L} + g_0 \mathbf{S}) | n' > |^2}{E_n - E_{n'}} \quad (2.2)
\]

The second term in equation 2.2 is the Van Vleck paramagnetic susceptibility. If the second term is small compared to the first, then the ground state energy can be rewritten via the Wigner-Eckhart theorem as

\[
< JLSJ_z | \mathbf{L} + g_0 \mathbf{S} | JLSJ'_z > = g_J(JLS) < JLSJ_z | \mathbf{J} | JLSJ'_z > . \quad (2.3)
\]

In the above, \( g_J \) is the Landé g-factor given by

\[
g_J(JLS) = \frac{3}{2} + \frac{1}{2} \left[ \frac{S(S+1) - L(L+1)}{J(J+1)} \right] \quad (2.4)
\]

if \( g_0 = 2 \). Once the energy of the system is determined, the magnetization and magnetic susceptibility may be calculated from

\[
M = - \frac{N}{V} \frac{\partial F}{\partial H} \quad (2.5)
\]

and

\[
\chi = \frac{\partial M}{\partial H} = - \frac{N}{V} \frac{\partial^2 F}{\partial H^2} \quad (2.6)
\]

In equations 2.5 and 2.6, \( F \) is the free energy which can be calculated from

\[
e^{-\beta F} = \sum_{J_z=-J}^{J} e^{-\beta g_J \mu_B H J_z}, \quad \beta = \frac{1}{k_B T} \quad (2.7)
\]

Using this, the magnetization may be written as

\[
M = - \frac{N}{V} g_J \mu_B J B J (\beta g_J \mu_B J H) . \quad (2.8)
\]
\( B_J(x) \) is the Brillouin function [Blundell (2001)] with \( x = \beta g_J \mu_B J H \).

\[
B_J(x) = \frac{2J+1}{2J} \text{coth} \left( \frac{2J+1}{2J} x \right) - \frac{1}{2J} \text{coth} \left( \frac{x}{2J} \right)
\]  

(2.9)

The Brillouin function is a hyperbolic tangent for a spin-1/2 system and evolves to the Langevin function

\[
L(x) = \text{coth} \, \frac{x}{2} - \frac{1}{x}
\]

(2.10)

for a classical, or infinite, spin system.

Often measurements are taken in the limit of small Brillouin \( x \), i.e., low field and high temperature. In both limits of \( J \) this results in a linear dependence of magnetization on field. Therefore, the magnetic susceptibility, \( \chi \), of non-interacting, free spins is given by Curie’s Law:

\[
\chi = \frac{C}{T}
\]

(2.11)

where \( C \) is the Curie constant, given below.

\[
C = N_A \frac{(g_J \mu_B)^2 J(J+1)}{3k_B}
\]

(2.12)

In many magnetically active samples, a plot of \( 1/\chi \) vs. \( T \) gives a straight line with positive slope, \( C \). Comparing the measured slope with the predicted response allows for the determination of an effective paramagnetic moment per ion or formula unit, \( p_{eff} \), defined as

\[
p_{eff} = g_J [J(J+1)]^{1/2}
\]

(2.13)

Doing so allows Eq. 2.12 to be rewritten as

\[
C = N_A \frac{p_{eff}^2 \mu_B^2}{3k_B}
\]

(2.14)

Usually, this form of the susceptibility is sufficient, however at low temperatures with sensitive measurements, it is useful to know the leading field correction to the free spin susceptibility.
Purely physical intuition would suggest that the application of an external field should reduce the susceptibility at a given temperature. A Taylor series expansion of hyperbolic cotangent gives

$$\coth x \approx \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + ...$$  \hspace{1cm} (2.15)$$

Since the magnetization is proportional to \(\coth(\alpha H)\), and the susceptibility is the first field derivative of magnetization, the leading correction to \(\chi\) due to magnetic field is proportional to \(-H^2\). It is therefore expected that the field dependent behavior of free spins will show an initial decrease in \(\chi\) as the field is increased.

When interactions between magnetic moments are significant, magnetic order can result. Depending on the nature and strength of the interaction ferromagnetism (all moments aligning in the same direction), antiferromagnetism (individual moments lie on one of two antiparallel sublattices with each sublattice carrying the same moment), or other types of magnetic structures can be realized at sufficiently low temperatures. A second effect of the interactions is to modify the paramagnetic Curie law behavior in susceptibility (Eq. 2.11) to a Curie-Weiss type given below.

$$\chi = \frac{C}{T - \theta}$$  \hspace{1cm} (2.16)$$

\(\theta\) is a characteristic temperature that may be positive or negative. Positive values for \(\theta\) generally give rise to ferromagnetic ordering, while negative values indicate antiferromagnetic order. The ordering temperature often is approximately equal to the absolute value of \(\theta\), however this is not always the case.

Ordering in local moment systems is usually modeled on an exchange interaction. The interaction of one moment with all of the others is assumed to be of a pairwise form with the energy of the interaction given by

$$U = -\Sigma J_{ij} S_i \cdot S_j$$  \hspace{1cm} (2.17)$$

where the sum is taken for \(i \neq j\). \(J_{ij}\) is called the exchange integral and its sign and magnitude determine the nature and strength of the interaction. The genesis of \(J_{ij}\) lies in the indistin-
guishability of the electrons and the fact that they are fermions. For $J_{ij} > 0$ the energy is minimized when the moments are parallel and ferromagnetic ordering is preferred. Often, only nearest neighbor interactions are considered which greatly simplifies the problem.

A second common simplification is the mean field approximation. In this model an individual moment interacts with an effective field produced by all of the other moments. The mean field model offers a simple method for explaining the Curie-Weiss law. If a magnetic field is applied to a sample of interacting magnetic moments, then within the mean field approximation the magnetization can be written as

$$M = \chi (H_{app} + H_{eff}) . \tag{2.18}$$

The effective field is assumed to be proportional to the magnetization ($H_{eff} = \lambda M$). Substituting this for $H_{eff}$ and replacing $\chi$ with a Curie law temperature dependence allows one to solve for $M(H,T)$.

$$M = \frac{CH}{T - C\lambda} . \tag{2.19}$$

This magnetization leads to a mean field susceptibility of

$$\chi = \frac{C}{T - C\lambda} \tag{2.20}$$

The above equation for $\chi$ predicts that the susceptibility should diverge as $T \to C\lambda$. Comparing 2.16 with 2.20 it is seen that $\theta = C\lambda$. Hence, it is also possible to determine the magnitude of the mean field parameter, $\lambda$, from a measurement of the paramagnetic susceptibility.

A connection between the mean field expression in Eq. 2.19 and the Brillouin or Langevin equations (Eqs. 2.9 and 2.10, respectively) can be made [Spaldin (2003)]. Taking the Langevin case the magnetization of a paramagnet can be written as

$$M = NmL(x) \tag{2.21}$$

where $x = mH/k_BT = \beta gJ\mu_B J H$. However, under the assumptions of the mean field the-
ory, the magnetization is also given by $M = H_{\text{eff}}/\lambda$. Further assuming that the field is given entirely by the molecular mean field implies the magnetization is a linear function of $T$. This follows from the expression for $x$ which shows that $H_{\text{eff}} = xk_BT/m$. This allows the magnetization to be written as

$$M = \frac{H_{\text{eff}}}{\lambda} = \frac{xk_BT}{m\lambda}$$

(2.22)

These two equations may be solved graphically for a given temperature to determine what values of $M$ are permitted. This is done for three different temperatures in Fig. 2.1. For all three temperatures, $M = 0$ is a solution. It is the only solution for high temperatures. When $T = T_C$ the slope of the linear mean field magnetization matches the initial slope of the Langevin paramagnetic function. For sufficiently low temperature, there are two solutions. The non-zero one is a result of the ordering. It is possible to relate the mean field parameter $\lambda$ with the ordering temperature. If Eq. 2.10 is differentiated with respect to $x$ it is seen that at $x = 0$ the slope of the curve is $Nm/3$, using the simplified $x$ given above. When the slope

![Figure 2.1](image-url)
of the linear curve matches this initial Langevin slope the temperature is $T_C$. Therefore, in
the Weiss mean field approach the ordering temperature is given by

$$T_C = \frac{Nm^2\lambda}{3k_B}. \quad (2.23)$$

The resulting mean fields for realistic saturation moments and ordering temperatures are $10^3$ T.
At the time Weiss introduced his theory it was unclear how such large fields could be generated.
Later, Heisenberg showed that the mean field does not really exist. Rather the ordering comes
from a combination of quantum mechanical and electrostatic exchange interactions between
the electrons. A very simple argument can be given to justify the existence of a magnetic
ordering from electrostatic effects. As the electrons are fermions, the pairwise wavefunctions
must be antisymmetric under exchange of the particle indices. Also, since each electron carries
the same charge there is a repulsive force between them. The electrostatic energy is minimized
by separating the electrons. An antisymmetric in space wave function is zero at the origin.
Such a function tends to maintain a separation between the two electrons. To satisfy the overall
antisymmetric nature of the paired wave function, the spin part must be the symmetric triplet
state for two spin-1/2 particles. Therefore, electrostatic interactions combined with quantum
mechanics allows for energy difference between magnetic states.

In metallic rare earth compounds exhibiting magnetic order the magnetic interaction is
often mediated by the conduction electrons via the Ruderman-Kittel-Kasuya-Yoshida (RKKY)
mechanism. In this interaction the local ionic moment polarizes the conduction electrons, and
this polarization oscillates as a function of distance. In this model the interaction, $J$, between
two local moments sitting at sites $\mathbf{R}_i$ and $\mathbf{R}_j$ is given by

$$J(\mathbf{R}_i - \mathbf{R}_j) \sim F(2k_F|\mathbf{R}_i - \mathbf{R}_j|). \quad (2.24)$$

In the above, $k_F$ is the Fermi wavevector and $F(x)$ is given by

$$F(x) = \frac{x \cos x - \sin x}{x^4} \quad (2.25)$$
In insulating compounds where there are no conduction electrons to mediate the exchange, order is communicated through the so-called ‘superexchange.’ The superexchange is a method whereby two magnetic ions separated by a non-magnetic ion interact. Even though the compound under consideration is an insulator, if the valence electrons can ‘hop’ from one ion to another they delocalize and lower their kinetic energy. This reduction due to delocalization is reminiscent of the particle in a box where the energy levels vary inversely with the linear dimensions of the box. In general, superexchange favors antiferromagnetism over ferromagnetism.

In ferromagnetically ordered samples application of a magnetic field of sufficient strength will saturate the moment. This occurs because all of the magnetic spins align with the field and there is no longer an increase in $M$ with increasing $H$. The sample moment can be divided into moment per spin, that is

$$M = N\mu_s.$$  

(2.26)

In strict local moment systems the saturated moment per ion will be the same as the effective paramagnetic moment per ion ($p_{eff}/\mu_s = 1$). Rhodes and Wohlfarth (1963) pointed out that

Figure 2.2  Plot of the RKKY function. Positive values correspond to ferromagnetic coupling while negative correspond to antiferromagnetic coupling.
this is not the case for all ferromagnets and used it to categorize magnetic materials. Some magnets are known to have much smaller saturation moments when compared with their paramagnetic moments. These are the candidate itinerant magnets, discussed in Ch. 4.

At zero kelvin a small bias field applied along the ordering axis is sufficient to completely saturate a ferromagnetic material as required by the third law of thermodynamics. In this case all of the local moments point in the same direction and the system is in its ground state. If the temperature is raised slightly the first change that occurs is one spin will flip so it points antiparallel to all other spins (provided a spin-1/2 system is considered). This is presumed to be the first excited energy state as the flipped spin will result in an increase in exchange energy and it represents the lowest increase available. Each spin in the lattice will have an equal probability of being the one that is flipped, so the location of the flipped spin is expected to wander about the lattice. The most probable mechanism for this traveling spin inversion is from neighbor to neighbor as the exchange force aligns the reversed spin. This propagation is a spin wave and only certain wavelengths are permitted based on the boundary conditions of the crystal. These long wavelength, low energy collective excitations reduce the low temperature magnetic moment more effectively than through considering single particle effects alone. In principle the effects of spin waves may be observable in TDR data, particularly frequency resolved data, but this is not the goal here. The present discussion of spin waves is motivated by a desire to understand collective excitations in itinerant systems as described by the spin fluctuations theory.

Working in a spin-1/2 system with \( z \) nearest neighbors, and considering the Hamiltonian to consist of the exchange term only,

\[
\mathcal{H} = -J \sum_{i \neq j} S_i \cdot S_j \quad (2.27)
\]

where \( S \) are the Pauli matrices it is possible to determine the energy spectrum of the spin waves. It is convenient to introduce to raising and lowering operators \( S^\pm \) defined by

\[
S^\pm_i = S_{2i} \pm iS_{yi} \quad (2.28)
\]
If $|\xi_\alpha\rangle$ represents the spin up state (with the z axis as the quantization axis) and $|\xi_\beta\rangle$ the spin down it can be shown that

\begin{align}
S^+|\xi_\beta\rangle &= |\xi_\alpha\rangle \\
S^+|\xi_\alpha\rangle &= 0 \\
S^-|\xi_\alpha\rangle &= |\xi_\beta\rangle \\
S^-|\xi_\beta\rangle &= 0 \\
S_z|\xi_\alpha\rangle &= \frac{1}{2}|\xi_\alpha\rangle \\
S_z|\xi_\beta\rangle &= -\frac{1}{2}|\xi_\beta\rangle
\end{align}

Therefore, the kets $|\xi_k\rangle$ are not eigenkets of the raising and lowering operators. The Hamiltonian (Eq. 2.27) can be rewritten as

\[ H = -J \sum_{i \neq j} \left[ \frac{1}{2} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + S_{zi} S_{zj} \right]. \] (2.35)

Based on the assumed ground state, its eigenfunction can be written as

\[ |\xi_0\rangle = |\xi_\alpha_1 \xi_\alpha_2 \xi_\alpha_3 \cdots \xi_\alpha_N\rangle \] (2.36)

Applying the Hamiltonian in Eq. 2.35 to this ground state gives

\[ H|\xi_0\rangle = -J \sum_{i \neq j} \left[ \frac{1}{2} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + S_{zi} S_{zj} \right] |\xi_0\rangle. \] (2.37)

The effect of the first two terms is to flip a reversed spin. Since there are no reversed spins in the ground state, these terms contribute nothing. Only the third term gives a non-zero result:

\[ H|\xi_0\rangle = -\frac{1}{4} N z J |\xi_0\rangle. \] (2.38)

Moving to the first excited state, with one reversed spin allows for a determination of the
reversal’s behavior. If the reversed spin is located at the $m$-th atom, the first excited state may be written as

$$|\xi_m> = |\xi_{\alpha_1}\xi_{\alpha_2}\cdots\xi_{\alpha_{(m-1)}}\xi_{\beta_m}\xi_{\alpha_{(m+1)}}\cdots\xi_{\alpha_N}>. \quad (2.39)$$

Operating on $|\xi_m>$ with Eq. 2.35 shows that all terms contribute to the new energy.

$$\mathcal{H}|\xi_m> = -J \sum \left[ \frac{1}{2} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + S_{zi} S_{zj} \right] |\xi_m> \quad (2.40)$$

The first two terms yield null vectors when operating on all spins except the $m^{th}$ and $(m+1)^{st}$. The last term has a nonzero contribution from the remaining $(N-2)$ spins given by

$$-J \sum S_{zi} S_{zj} |\xi_m> = -\frac{1}{4} J z (N-2) |\xi_m> \quad (2.41)$$

where the $z$ on the right hand side is the number of nearest neighbors. Taking the remaining spins with the first two terms in Eq. 2.40 gives

$$-J \sum_{i=1}^{z} \frac{1}{2} \left( S_{m}^+ S_{m+1}^- + S_{m}^- S_{m+1}^+ \right) |\xi_m> = -\sum_{i=1}^{z} J |\xi_{m+i}>. \quad (2.42)$$

The sum in the above equation is over the $z$ nearest neighbors. The result is like this because the second term gives a null vector again, but the first term moves the reversed spin by one site. The $S_{zi} S_{zj}$ term contributes an energy of

$$\frac{1}{2} J z |\xi_m> \quad (2.43)$$

when operating on the $m^{th}$ and $(m+1)^{st}$ spins. The net result is

$$\mathcal{H}|\xi_m> = \left( -\frac{1}{4} J N z + z J \right) |\xi_m> - \sum_{i=1}^{z} J |\xi_{m+i}>. \quad (2.44)$$

It is obvious that $|\xi_m>$ is not an eigenfunction of $\mathcal{H}$. The effect of the hamiltonian is to move the reversed spin, allowing it to propagate through the lattice. Therefore an eigenfunction of
$H$ may be formed by a linear combination of the $N$ functions represented by $|\xi_m>$, or

$$|\Xi> = \sum c_m |\xi_m>.$$  \hspace{1cm} (2.45)

The coefficients $c_m$ are given by

$$c_m = A_m e^{ik \cdot R_m}$$  \hspace{1cm} (2.46)

where $R_m$ is the position vector of atom $m$. Imposing periodic boundary conditions ($c_m = c_{m+N}$) the components of $k$ are confined to particular values. This is analogous to the classic particle in a box problem with solutions of the sort

$$k_i N_i x_{mn} \frac{2\pi}{2\pi} = 0; \pm 1; \pm 2; \cdots$$  \hspace{1cm} (2.47)

$N_i$ is the number of lattice sites along the $i$ direction and $x_{mn}$ is the distance between those sites. The eigenfunctions have wavelike properties and operating on Eq. 2.45 with Eq. 2.35 gives

$$H|\Xi> = E|\Xi> = (E_0 + zJ) |\Xi> - J \sum e^{ik \cdot r} |\Xi>.$$  \hspace{1cm} (2.48)

$r$ is the vector between the reversed spin and one of its nearest neighbors, and the sum is taken over all nearest neighbors. The energy of the spin wave is

$$E - E_0 = J(z - \sum e^{ik \cdot r}).$$  \hspace{1cm} (2.49)

For small $k$ (low energy) this gives

$$E - E_0 = \frac{1}{2} J \sum (k \cdot r)^2.$$  \hspace{1cm} (2.50)

For lattices with cubic symmetry this reduces to

$$E - E_0 = Jk^2 a^2$$  \hspace{1cm} (2.51)
where $a$ is the lattice spacing. Comparing this with the usual quantum mechanical energy for a wave implies that

$$\hbar \omega = J k^2 a^2 \quad (2.52)$$

Since the TDR is a measure of the ‘bulk’ susceptibility, it is not feasible to try to map out spin-wave dispersion relations. However, if a material exhibits gaps in its spin wave spectra, it may be possible to detect these gaps with frequency resolved measurements.

The free energy of a system is the difference between the internal energy and the entropic energy.

$$F = U - TS - \mathbf{M} \cdot \mathbf{H} \quad (2.53)$$

Various derivatives of the free energy correspond to different thermodynamic quantities. Entropy is the first derivative of the free energy with respect to temperature, and heat capacity is the second. Of particular interest for magnetic systems is the magnetic energy $\mathbf{M} \cdot \mathbf{H}$. The negative of the first derivative of $F$ with respect to $H$ gives the magnetization, $M$.

$$- \frac{\partial F}{\partial H} = M \quad (2.54)$$

Taking the derivative of $M$ with respect to $H$ gives the magnetic susceptibility, $\chi$.

$$\chi = \frac{\partial M}{\partial H} = - \frac{\partial^2 F}{\partial H^2} \quad (2.55)$$

Experimentally it is seen that certain thermodynamic quantities either grow very rapidly in the vicinity of a phase transition or have a step-wise change at $T_c$. The transition is classified based on which derivative (first, second, third, etc.) of the free energy this rapidly growing quantity is. The para- to ferromagnetic phase transition is second order, so the magnetic susceptibility is one of the diverging quantities. Application of a small field will tend to weakly align the moments in the direction of the field. As the temperature approaches $T_C$ the exchange interaction grows in importance relative to the thermal randomization, and the alignment of a few moments in one direction will induce other moments to align as well. Thus,
for a given applied field the response of the magnetization is amplified when compared to the non-interacting case. The mean field theory derivation of the magnetic susceptibility leading to the Curie-Weiss law accurately recreates this divergence. This is a tautology in some sense, as Weiss developed his theory to account for the magnetic order and rapidly growing susceptibility at the transition temperature.

Adhering to the ferromagnetic case, applying a magnetic field will suppress the growth of $\chi$ near the phase transition, turning it into a local maximum near $T_c$. Further, the applied field shifts the maximum to higher temperatures. The DC field adds an additional Zeeman energy to the problem which makes it easier for the moments to order resulting in the shift in temperature. Further, the energy splitting between the spins parallel and antiparallel to the field makes it more difficult for a perturbing field to induce a change in magnetization. This is what causes the suppression in $\chi$.

Landau developed a very simple model to show how a second order phase transition can occur [Landau (1937)]. He assumed there was a phase transition at some temperature, $T_c$, characterized by an ‘order parameter.’ The order parameter is some quantity that is zero for $T > T_c$ and continuously grows from zero to some saturation value as the temperature is lowered below $T_c$. Associated with the order parameter is a conjugate field. In general terms, the response of an order parameter to changes in its conjugate field is termed the susceptibility. In ferromagnets the order parameter is the magnetization. The field conjugate to magnetization is the magnetic field, $H$. The response of the magnetization to changes in the applied field is the usual susceptibility, $\chi$. If $M_s$ is taken as the saturation value then the reduced order parameter, $m$, and the reduced temperature, $t$, can be defined as

$$ m = \frac{M(T)}{M_s} $$

(2.56)

and

$$ t = \frac{T}{T_c} $$

(2.57)

For $t < 1$ the system is in the low symmetry, ordered phase, while for $t > 1$ it is in the
high symmetry, disordered phase. If we are concerned with magnetization, the energy of the system cannot depend on whether \( m \) is positive or negative. These only indicate the direction the magnetization points relative to an arbitrary reference. Assuming the free energy can be expressed as a polynomial in \( m \), symmetry requires that no odd powers of \( m \) appear. The free energy can then be written as

\[
F(t, m) = F_0(t) + A(t)m^2 + \frac{1}{2}B(t)m^4. \tag{2.58}
\]

The prefactor of \( 1/2 \) on the quartic term is placed for later convenience. \( F_0(t) \) contains all temperature dependence not associated with the magnetization. In order to determine the equilibrium value of \( m \), the free energy must be minimized with respect to \( m \). Thus, \( \partial F / \partial m = 0 \) and \( \partial^2 F / \partial m^2 > 0 \).

\[
\frac{\partial F}{\partial m} = 2A(t)m + 2B(t)m^3 = 0 \tag{2.59}
\]

\[
\frac{\partial^2 F}{\partial m^2} = 2A(t) + 6B(t)m^2 > 0 \tag{2.60}
\]

From Eq. 2.59 \( m = 0 \) and \( m^2 = -A(t)/B(t) \) are the two solutions. If \( m = 0 \), then Eq. 2.60 requires \( A(t) > 0 \) to assure a minimum. This corresponds to the case when \( t > 1 \). If \( m \neq 0 \) then substitution of \( -A(t) = B(t)m^2 \) into the second derivative shows that \( A(t) < 0 \) to assure a minimum in \( F \). This is the case when \( t < 1 \). Therefore, it is seen that as \( t \) is lowered through 1, \( A(t) \) changes sign from positive to negative. Any functional form of \( A(t) \) that satisfies this one condition will be sufficient to reproduce the phase change. Landau assumed a very simple temperature dependence for \( A \),

\[
A(t) = \alpha(t - 1). \tag{2.61}
\]

With this the magnetization for \( T < T_c \) is given by

\[
m = \pm \sqrt{\frac{\alpha(1-t)}{B(t)}}. \tag{2.62}
\]

The \( \pm \) indicates the isotropic nature of space. “Up” magnetization is equivalent to “down”
in the absence of an applied field. Landau further assumed that \( B(t) = B \) is constant with temperature. Under this assumption, the magnetization grows as \( t^{1/2} \) near \( t = 1 \). This also allows the free energy to be expressed in terms of \( \alpha \) and \( B \).

\[
F = F_0(t) - \frac{\alpha^2(t - 1)^2}{2B}
\]  

(2.63)

From this expression for the free energy the magnetic contribution to the entropy and the heat capacity is easily computed. Landau’s theory predicts a jump in heat capacity at \( T = T_c \).

Since everything regarding the phase transition up to now has been derived in zero applied field, it is not possible to predict the behavior of the susceptibility as a function of temperature. This can be overcome by adding a small magnetic Zeeman term \( (-m h \text{ where } h = H_{\text{app}} M_s) \) to Eq. 2.58. The smallness of the Zeeman energy is ensured by keeping \( h \) very close to zero.

The textbook approach in this case [Pathria (1996)] is to rewrite Eq. 2.58 including \( h \), set the derivative of \( F \) with respect to \( m \) equal to zero and then solve for \( h \).

\[
h = 2A(t)m + 2Bm^3.
\]  

(2.64)

From here the inverse susceptibility \( (1/\chi) \) is defined as \( \partial h / \partial m \) which gives

\[
\chi^{-1} = 2A(t) + 6Bm^2.
\]  

(2.65)

For \( t > 1 \), \( m = 0 \) and \( \chi \) diverges like \( 1/t \) as \( t \to 1^+ \) if the form of \( A(t) \) found in the zero field case holds. For \( t < 1 \), \( m = \sqrt{\alpha(1-t)/B} \). Substituting this in for \( \chi \) gives that the susceptibility diverges as \( 1/t \) as \( t \to 1^- \). The last bits of information gleaned from this procedure come from considering what happens to \( m \) if \( h \) is varied when \( t = 1 \). From Eq. 2.64 it is seen that \( m \propto h^{1/3} \) in the low field limit. This in turn implies that at \( t = 1 \), that is at the actual zero field phase transition temperature, the susceptibility should vary with field like \( \chi \propto h^{-2/3} \).

The most significant conclusion drawn from the Landau theory is that the physically measurable quantities \( m \) and \( \chi \) vary with power law dependencies on \( t \) and \( h \) in the vicinity of the
phase transition. Based on the temperature dependence of $\chi$ it is seen that the Landau theory of phase transitions is a mean field type of calculation. Therefore, any arguments derived from it are subject to the limitations of mean field theory.

The Heisenberg interaction that models long range magnetic order is isotropic (Eq. 2.17). However, in many magnetically ordered materials the spontaneous magnetization prefers to lie along particular crystallographic directions. This phenomenon is termed magnetocrystalline anisotropy (MCA). The most common manifestation of MCA is in the applied field required to saturate the measured magnetic moment of a sample. The direction that requires the smallest field for saturation is termed the “easy” axis. Other directions are called “hard” axes. The microscopic origin of this effect is in the interaction of the magnetic moments with their crystalline electric field environments.

Models of MCA are based around the idea that when the magnetization lies along the easy axis, the free energy of the system is minimized (if domain effects are neglected). The moment must be forced away from the easy axis which increases the energy in the sample. The connection between the energy increase and the displaced angle is made via anisotropy constants. Determining these constants can be accomplished in several ways. Commonly one measures the work required to saturate the magnetic moment of a sample along different directions. Then it is possible to extract the relative values of the constants. Another method exploits the fact that a moment placed in a perpendicular magnetic field will precess about the field with a characteristic frequency. If an alternating field with this frequency is applied perpendicular to the static field, there will be a coherent absorption of energy which manifests itself (among other ways) as a dramatic increase in the susceptibility of the sample. Such transverse measurements have been shown to be useful in determining the anisotropy constants for thin films [Spinu et al. (2000)]. A third method is to fix $H$ and measure $M$ as a function of angle, rotating about symmetry axes in the sample. Then, fitting the data to an appropriate model will give the anisotropy constants.

Experimentally it is observed that the magnitude of anisotropy constants strongly depend on temperature [Morrish (2001)]. A major shortcoming of the typical techniques employed to
measure the anisotropy constants is a fairly large static field must be applied. Such a field can, and does, introduce considerable energy, especially at low temperatures and in samples with a large moment per ion. A 10 kOe field applied to a single Bohr magneton moment induces a Zeeman splitting on the order of 1 K. Especially along the hard directions, this field may not be sufficient to saturate the moments. Indeed, it is not uncommon that a 55 kOe field is insufficient to perform a saturation measurement at 2 K.

To develop a feel for the MCA, three systems are considered, iron, nickel, and cobalt. Iron and nickel both possess cubic symmetry. The easy direction for iron is along the cube edge and for nickel it is the body diagonal. Cobalt is hexagonal and manifests uniaxial anisotropy with the c axis being the easy direction and anywhere in the hexagonal planes being (nearly) equivalent hard directions [Morrish (2001)]. These cases are studied because they illustrate the principle, but due to the high degree of symmetry many terms may be neglected. Deviations from the easy axis will increase the energy. It is convenient to express the anisotropy energy as a power series of trigonometric functions of the angles the magnetization direction makes with the crystal axes.

Beginning with the cubic systems, the direction cosines from the cube axes may be denoted as $\alpha_1$, $\alpha_2$, and $\alpha_3$. The expression for the anisotropy energy must be independent of the sign of the $\alpha$'s. Hence, only even powers will appear. Cross terms of the type $\alpha_1 \alpha_2$ are also not permitted. The first candidate is the term $k_1 \alpha_1^2 + k_2 \alpha_2^2 + k_3 \alpha_3^2$. However, this term will not give any anisotropy energy as the expression must be independent of an interchange of any two $\alpha$'s which is a manifestation of the freedom in choosing two of the three directions in a right-handed coordinate system. Therefore, $k_1 = k_2 = k_3$. Since $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$ there will be no contribution to the anisotropy from this term. This means the lowest order term is the fourth degree term. Again, there is a simplification. Only the term containing $\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2$ needs to be considered because it is equal to $\frac{1}{2} - \frac{1}{2} (\alpha_1^4 + \alpha_2^4 + \alpha_3^4)$. The next term will be of degree 6. Generally this is sufficient to explain the experimental results. Thus, the anisotropy
energy for a cubic system may be written as

\[
U_{\text{cubic}}^{\text{aniso}} = K_1 \left( \alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2 \right) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2. \tag{2.66}
\]

Three typical cases are considered. First, if the magnetization lies along a cube edge, then two of the three \(\alpha\)’s are zero and the total energy is zero regardless of \(K_1\) and \(K_2\). Second, if the magnetization lies along a body diagonal, \(\alpha_1 = \alpha_2 = \alpha_3 = \sqrt{2}/2\). The anisotropy energy in this case is given by

\[
U_{\text{aniso}} = \frac{3K_1}{4} + \frac{K_2}{8}. \tag{2.67}
\]

If \(K_1\) is negative and \(K_2 < -\frac{3K_1}{2}\) then the body diagonal will be the easy axis. Finally, if the magnetization lies along a face diagonal, then one of the \(\alpha\)’s is zero and the anisotropy energy is \(\frac{K_1}{4}\). If \(K_1 < 0\) and \(K_2 > -\frac{3K_1}{2}\) then the face diagonal will be the easy axis. From the latter two cases, it may be seen that if \(K_1 > 0\) then the cube edges will be easy directions.

For uniaxial symmetry, only one angle is needed. Specifically, if \(\theta\) is defined as the angle between the magnetization and the easy axis then the anisotropy energy may be written as

\[
U_{\text{uniso}}^{\text{aniso}} = K_1' \sin^2 \theta + K_2' \sin^4 \theta. \tag{2.68}
\]

Taking the uniaxial case, if a magnetic field is applied at an angle \(\phi\) (Fig. 2.3) with respect to the easy axis, the magnetization will be deflected to that direction. Neglecting the fourth order term (small \(H\)) the total energy of the system is expressed as

\[
U_{\text{total}} = K_1 \sin^2 \theta - MH \cos (\phi - \theta). \tag{2.69}
\]

The equilibrium condition is met when \(U_{\text{total}}\) is minimized, i.e. \(dU/d\theta = 0\).

In general, this anisotropy should manifest itself in the measurement of magnetic susceptibility. It is found that this is true, particularly in the vicinity of the phase transition. This indicates that the anisotropic exchange leading to the magnetic order persists up to and above the ordering temperature. Measurements with the excitation field parallel to the ordering
axis give a much stronger signal when compared to a measurement perpendicular to the easy direction. This is discussed in more detail below.

2.3 Materials Studied and Results

Experimentally the TDR data on local moment ferromagnets in the vicinity of the phase transition show a narrow well defined peak in $\chi$. Application of a dc magnetic field suppresses this peak and shifts it to higher temperatures. In systems with significant magnetic anisotropy, the orientation of the crystal with respect to the rf probe field affects the behavior of the observed peak at and above $T_C$ (Sec. 2.5). It is useful to compare these data with more conventional means like low field dc magnetization, low frequency ac susceptibility, resistivity, and heat capacity. To this end, single crystals of the ferromagnetic CeVSb$_3$ [Sefat et al. (2008)] with a Curie temperature of 4.6 K were studied using these more common techniques.

Figure 2.4 presents the heat capacity measured on a Quantum Design Physical Properties Measurement System (PPMS) and magnetic susceptibility as measured by the $^4$He TDR in
zero applied magnetic field for a single crystal of CeVSb$_3$ (Sec. 2.3.2). There is a clear lambda like anomaly in heat capacity at approximately 4.6 K. This coincides with a dramatic peak in $\chi$. The coincident temperatures strongly suggest that the peak in $\chi$ is associated with the phase transition. The gradual decrease in measured susceptibility for temperatures less than 4.3 K or so is associated with a decrease in resistivity. The peak in $\chi$ should be contrasted with the response of antiferromagnetic SmAgSb$_2$ (Fig. B.1). For the antiferromagnet there is no corresponding increase in $\chi$ at the Néel temperature. Rather there is just a decrease in resistivity due to a loss of spin disorder scattering as the samarium moments order. Figure 2.4 Comparison of heat capacity (left axis, black circles) and TDR magnetic susceptibility (right axis, red squares) for CeVSb$_3$ measured along the magnetic easy axis. Peaks occur in both data sets at the ordering temperature.

Figure 2.4 Comparison of heat capacity (left axis, black circles) and TDR magnetic susceptibility (right axis, red squares) for CeVSb$_3$ measured along the magnetic easy axis. Peaks occur in both data sets at the ordering temperature.

2.5 compares low frequency ac susceptibility available from a commercial ac susceptometer (Quantum Design Magnetic Properties Measurement System, or MPMS) with the same resonator data from Fig. 2.4. Both data sets are normalized to the maximum in measured $\chi$. For both systems, this maximum corresponds to precisely the same temperature to within 50 mK. The drive frequency from the commercial system was set at 333 Hz and the peak to peak amplitude of the probe field was 1 Oe. On the paramagnetic side, the normalized data
from both systems follows the same temperature behavior. However on the ferromagnetic side the low frequency data drops off much slower than that from the resonator. This is due to a combination of the frequencies and the amplitudes of the probe fields. The TDR data are derived from a probe field $\leq 10$ mOe which is at least 100 times smaller than the commercial system’s. It is expected that correlation effects should dominate the response of the sample since the TDR provides such a weak perturbation. Also the much higher frequency from the TDR ($\sim 10^5$ times larger) cuts off the magnetic response of slower relaxation processes. This naively can be thought of as analogous to a simple harmonic oscillator. If the oscillator is driven far above its resonant frequency, then the response is very limited in amplitude. The oscillator is very ‘stiff’ at the high frequencies. Figure 2.6 shows the zero field cooled-field

![Graph showing comparison of low frequency ac susceptibility (solid square) and TDR data (hollow hexagons) for CeVSb$_3$. Both curves are normalized to 1 at the maximum.](Image)

Figure 2.5 Comparison of low frequency ac susceptibility (solid square) and TDR data (hollow hexagons) for CeVSb$_3$ with the probe field aligned with the magnetic easy axis. Both curves are normalized to 1 at the maximum.

warmed static susceptibility, as defined as magnetic moment divided by applied field, versus temperature in a 25 Oe field for CeVSb$_3$. The field is applied along the magnetic easy axis. As
this is a zero field cooled measurement, there are magnetic domains present. On warming in
the applied field, thermal energy assists in domain wall motion allowing the moment parallel
to the field to grow. At $T_C$ thermal energy dominates the exchange interaction leading to order
and the moment drops. The paramagnetic dc susceptibility is qualitatively similar to both the
low frequency ac susceptibility and the TDR data. Again, it is in the ferromagnetic state that
these data differ dramatically.

Also shown in Fig. 2.6 are resistivity with the current parallel ($J||c$) and perpendicular to
($J||b$) the magnetic easy axis in zero field. Of particular importance is the lack of a peak in the
resistivity at $T_C$. Comparison with the TDR data shows that below $T_C$ the rf susceptibility
is dominated by the resistivity, while above $T_C$ there is a mixing of the spin susceptibility
and the resistivity components. In the case where the TDR probe field is aligned with the
crystallographic c axis, the resistivity in the ab-plane is simultaneously probed. The convex
nature of the b axis $\rho$ is masked in the TDR data by the increasing spin susceptibility as
$T \to T_C$.

Figure 2.6  Zero field cooled static susceptibility (left axis) and resistivity
for current applied along the c and b crystal axes (right axis)
for CeVSb$_3$. 
Several experimental facts are clear from these measurements on CeVSb₃. First, the TDR probes a combination of spin and resistive contributions to susceptibility. Second, in the vicinity of a ferromagnetic phase transition the spin susceptibility dominates the change in measured $\chi$, but it does not necessarily dominate the absolute value of $\chi$. Third, the peak in $\chi$ is associated with the magnetic ordering as evidenced by the overlapping temperature ranges for both the TDR data and heat capacity. Finally, the peak from the TDR measurement is much sharper than the low frequency commercial measurement of susceptibility.

Applying a dc magnetic field suppresses $\chi$ in amplitude and shifts it to higher temperatures, as seen in Fig. 2.7. This is the situation where the ac and dc fields coincide with the eventual magnetic easy axis. To try to more clearly elucidate the nature of this response, a powder sample of the cubic insulating ferromagnet EuS ($T_C \approx 15$ K) was also measured. A small amount of commercially obtained powder was mixed with low temperature grease and placed
on the end of the sample holder. Measurements of $\chi$ vs. $T$ were taken in different dc magnetic fields. The results are shown in Fig. 2.8. The contrast between the measured susceptibility

![Diagram](image.png)

Figure 2.8 $\chi$ vs. $T$ for powdered EuS. Numbers next to curves indicate the applied dc field in kOe.

in powdered EuS and single crystal CeVSb$_3$ is stark. However, comparison of the zero field response reveals some obvious similarities in the paramagnetic phase. Both show a substantial relative increase in $\chi$ beginning at about $1.5T_C$. At the Curie temperature the cerium compound shows a dramatic drop in $\chi$ while the europium compound maintains a large, nearly constant susceptibility. The behavior of the powder sample can be understood by thinking of the sample as a superparamagnetic specimen. In this case, the individual powder grains act like single macrospins with a large moments. The low magnetocrystalline anisotropy in EuS allows the ordered moments to rotate nearly freely with respect to the crystal axes resulting in the large zero field susceptibility. In general, superparamagnetic behavior assumes uniform grain size and shape to facilitate analysis. This is not attempted here, nor are the assumptions checked.

The in field behavior is also quite similar on the paramagnetic side. While the single crystal sample shows a peak in zero field that becomes a broadened and suppressed maximum, the
powder develops a broad maximum that suppresses with applied field. Both maxima (single crystal and powder) shift to higher temperatures as the field is increased. In the single crystal there is no strong feature in $\chi$ at $T_C$ in applied fields. However, the powder shows a sharp break in slope, evolving to a minimum as the field increases. This can be ascribed to the transition from a field induced ordering for temperatures greater than $T_C$ to actual ordering and collective behavior amongst the grains for $T < T_C$.

The main conclusion to be drawn from a comparison of these two samples is that in simple local moment ferromagnets, there should be a strong increase in $\chi$ for $T > T_C$. It will also be shown that the peak behavior is quite general for single crystal samples, including the insulating YTiO$_3$. If there is other observed behavior, it is likely that there is deviation from the simple ferromagnetic ordering. The converse, single crystal behavior consistent with CeV$_3$Sb$_3$, does not necessarily imply simple ferromagnetic ordering, though.

2.3.1 Multiple Magnetic Phases in CeSb

As an example of the utility and sensitivity of the TDR the $H - T$ phase diagram of CeSb was determined solely from measurements of $\chi_{ac}$ using the $^3$He. CeSb has been well studied and is known to manifest a complex magnetic phase diagram. It forms a layered structure with magnetic ordering occurring in some of the layers while others remain paramagnetic as determined via heat capacity [Roussat-Mignod et al. (1980)] and neutron diffraction [Lebech et al. (1980)].

Figure 2.9 shows a temperature scan for the compound CeSb in zero applied field. This compound is well known to have multiple magnetically ordered phases in field-temperature space [Wiener and Canfield (2000)]. The TDR reproduces the phase diagram presented therein (see Fig. 2.10) as well as those reported previously [Bartholin et al. (1975), Meier et al. (1978), Roussat-Mignod et al. (1980), Escorne et al. (1981)]. Each transition into a new phase results in a kink in the measured susceptibility. This kink may originate in either the resistive or spin contributions to susceptibility. Either way, the transition would be observed.

The phase diagram developed by the TDR was generated by measuring $\chi$ parallel to the
Figure 2.9

Plot of difference between TDR resonant frequency, $f_{\text{res}}$, and a fixed local oscillator, $f_{\text{LO}}$ versus temperature in zero applied magnetic field. This difference is proportional to $\chi$. As described in the text, $f_{\text{LO}} > f_{\text{res}}$. Inset shows the derivative of the main plot. The small peak near 3 K in the derivative plot is from the superconducting transition of a small amount of tin flux left from the crystal growth.
c axis of the sample. This means the resistivity in the ab plane was probed. Further, only temperature sweeps were performed in constant magnetic field. These facts taken in tandem can account for the missed lines in the TDR data, however it does not account for the observed lines not seen in other data. The general nature of this difference was not explored, rather the measurement was performed as a check on the capabilities of the TDR. The strong similarities between the published and measured phase diagram clearly demonstrate that this apparatus can be applied to more systems than just superconductors.

![Figure 2.10 Phase diagram for single crystal CeSb. Hollow points are from Wiener and Canfield (2000) while solid points are TDR data.](image)

### 2.3.2 CeVSb$_3$

CeVSb$_3$ is the only member of the RV$\text{vsb}_3$ family to manifest ferromagnetic order [Sefat et al. (2008)]. The Curie temperature for this compound is 4.6 K (Fig. 2.4), and it has a saturated moment of 1.4 $\mu_B$ per cerium. It crystallizes in an orthorhombic structure with lattice parameters $a \approx 13.17\text{Å}$, $b \approx 6.24\text{Å}$, and $c \approx 6.02\text{Å}$. The magnetic easy axis is the
crystallographic $c$ axis. Room temperature resistivity is on the order of 125 $\mu\Omega$ cm and decreases to less than 50 $\mu\Omega$ cm at 2 K. Therefore, unless the sample is reasonably large ($\geq 0.75$ mm on a side), the measured $\chi$ should not have a resistivity component. Data collected on two samples (one in the $^3$He and one in the $^4$He TDR) do indeed show that for small samples this is true. The larger $^4$He sample used to study anisotropy gives a much larger low temperature suppression from the resistive component. This is more evident when the strong magnetic ordering peak is suppressed via an applied field. The smaller $^3$He sample does show a slight resistive tail for $T < T_C$, but it is much reduced compared to the $^4$He system.

2.3.3 CeAgSb$_2$

CeAgSb$_2$ is a member of the tetragonal $R$AgSb$_2$ family. Published values of the lattice parameters obtained from the gadolinium member show that $a \approx 4.29\,\text{Å}$ and $c \approx 10.49\,\text{Å}$. It is known to order ferromagnetically along the $c$ axis at 9.8 K with a saturated moment of 0.37 $\mu_B$ per cerium, which is greatly reduced from the paramagnetic effective moment of 2.26 $\mu_B$ per cerium [Myers et al. (1999b)]. The large ratio between $p_{\text{eff}}$ and $\mu_{\text{sat}}$ would put this on the possible list of itinerant moments when compared with the Rhodes-Wohlfarth plot. However, in Myers et al. (1999b) it is shown that strong crystalline electric field effects constrain the moments of the other magnetic $R$AgSb$_2$ to the basal plane. Anisotropic magnetization data vs. applied field in the cerium compound suggests that there may be antiferromagnetic ordering in the plane with a cant of the moment out giving rise to the small observed c-axis saturation value. A magnon model of the temperature dependence of the resistivity lends support to this idea that there is in-plane antiferromagnetic order [Jobiliong et al. (2005)]. Unpublished magneto-optic Kerr imaging of CeAgSb$_2$ suggests that the material has rectangular tube domains organized into superdomains. Magnetization loops vs. field show that reducing the field after saturation leads to sharp change in moment at approximately -60 Oe after which $M(H)$ follows the virgin curve.

Fig. 2.12 is a detail of how the peak in $\chi$ suppresses with applied field. The full amplitude change in $\chi$ is less than $2 \times 10^{-3}$ in cgs units for zero field. For the lower fields, the $\chi$ vs. $T$
Figure 2.11 Zero field $\chi$ for CeAgSb$_2$.

Figure 2.12 $\chi$ near $T_C$ in the labeled applied fields (in Oe) for CeAgSb$_2$. Note the extreme narrowness of the peak.
curves merge by just under 9.6 K. However, the 1 kOe curve shows measurably lower $\chi$ from 10 K and down. There are two possibilities as to what is causing the reduction in the observed susceptibility. The first is that the applied field is suppressing the spin fluctuations associated with the phase transition. While this is clearly the case, since the peak in $\chi$ marking $T_C$ is caused by these fluctuations, this suppression is achieved by a field of 200 Oe. The second possibility is that there are ordered state magnetic fluctuations which are suppressed. This possibility was considered by Jobiliong et al. (2005). If this is the case, then the observed decrease in $\chi$ should be evident in $\rho$ as well, as the effect of the fluctuations was to provide an additional scattering mechanism to allow for a unique resistivity curve.

![Figure 2.13](image)

Figure 2.13  $\chi$ vs. $T$ for CeAgSb$_2$ in four fields $\pm 60$ Oe and $\pm 100$ Oe.

To verify that the behavior of the peak in $\chi$ at $T_C$ is not affected by any stray fields, temperature dependent data on CeAgSb$_2$ was collected in both positive and negative fields or 60 and 100 Oe. The results in Fig. 2.13 clearly show that there are no stray fields on the order of 60 Oe or greater.
2.3.4 YTiO$_3$

YTiO$_3$ is a perovskite oxide that orders ferromagnetically at approximately 23.5 K. Each titanium ion carries a small moment of 0.85 $\mu_B$ [Garrett et al. (1981)]. The crystallographic c axis is the magnetic easy axis. This insulating material exhibits orbital ordering in the ferromagnetic state [Sawada et al. (1997), Itoh et al. (1999), Akimitsu et al. (2001), Iga et al. (2004), Ito et al. (2004)], but there is an argument against the proposed orbital structures [Ulrich et al. (2002)]. What is not in dispute is the ferromagnetic ordering, which is of paramount concern here.

Figure 2.14 presents $\chi_{ac}$ vs. temperature in several applied fields for YTiO$_3$ measured parallel to the c-axis. The general features near the phase transition seen here are common to both CeVSb$_3$ and CeAgSb$_2$. The low temperature behavior is likely due to the orbital ordering effects under debate in the not too distant past.

![Figure 2.14](image.png)

Figure 2.14 $\chi_{ac}$ in arbitrary units of insulating YTiO$_3$ measured along the ferromagnetic easy axis (crystallographic c-axis).

As an insulating magnetically ordered compound it is expected that the measured susceptibility be positive through the transition. As has been presented previously, this is not the case for metallic ferromagnets wherein the resistive screening forces the measured $\chi$ to be negative.
even though the system is transitioning to the ordered state. Fig. 2.15 shows the measured susceptibility obtained from the TDR. As expected, the observed $\chi$ is positive. Further the zero field change in $\chi$ at $T_C$ is approximately 7 times larger than zero field change in $\chi$ at $T_C$ for CeAgSb$_2$

![Graph showing susceptibility against temperature](image)

Figure 2.15 $\chi_{ac}$ in cgs units for YTiO$_3$.

### 2.3.5 Gd

Elemental gadolinium undergoes a para- to ferromagnetic phase change at $T_C \approx 294$ K carrying a full 7.55 $\mu_B$ per ion [Nigh et al. (1963)]. It has a hexagonal crystal structure with the magnetic easy axis along the c axis as determined by neutron scattering experiments [Cable and Wollan (1968)]. There is also a spin reorientation transition that occurs at $T_{SR} \approx 235$ K wherein the magnetic moments gradually rotate away from c to about 65° at 180 K and then back toward c at lower temperatures, finally settling at about 30° from the c axis. Normally the spin-only moment from the half-filled 4$f$ shell would be relatively unaffected by crystal electric field effects, and most gadolinium compounds are fairly isotropic. However, large dipolar
coupling effects can also give rise to anisotropy. This is believed to be the case for gadolinium [Srinath et al. (1999)]. It has been proposed that the actual order for $T_{SR} < T < T_C$ is not truly ferromagnetic, but rather a long-period ($\sim 70$ Å) sinusoidally modulated spin structure on the basis of low frequency ($f \leq 1$ kHZ) ac susceptibility measurements [Coey et al. (2000)]. This conclusion was formed based on the observation that the ac susceptibility does not go through an absolute maximum at $T_C$. Rather, the largest value of $\chi$ is observed at $T_{SR}$.

TDR data on a single crystal of Gd was collected in the $^4$He system. The design of the system is not optimized for heating a sample from 2 K up to room temperature. Reducing the ramp rate on the heater still results in considerable lag between the sample and thermometer temperatures. Characterization of a sample based on high temperature transitions is not reliable with the current set up. However, if a sample with known transitions is measured, the existence and field dependent behavior of those transitions can be examined in a qualitative manner. A second complication in evaluating the precise behavior in the vicinity of the Curie temperature in this compound is the uncertainty in the temperature. Negative temperature coefficient thermometers, like that employed in this setup, have very flat resistance vs. temperature curves near $T \approx 300$ K. This coupled with the aforementioned lag suggests that measured temperatures have an uncertainty on the order of at least $\pm 1\%$.

Bearing this in mind, Fig. 2.16 shows $\chi$ vs. reduced temperature for Gd in four applied fields. The zero field curve clearly shows a high temperature peak which is consistent in shape with a lower frequency feature seen at $T_C$ [Dan’kov et al. (1998), Coey et al. (2000)]. Temperatures are normalized to the temperature of the zero field peak. At lower temperatures there is a knee followed by an ill-defined maximum. The lowest temperature feature is most likely observed at the correct temperature and is likely an indicator of the spin reorientation transition. As the applied field is increased, the high temperature peak is suppressed in amplitude. This is consistent with what is observed in all other local moment ferromagnets. Thermally, it appears that the peak shifts to lower temperatures as the applied field increases (Fig. 2.17). For all applied fields this trend persists, however the shift is on the order of the estimated uncertainty making it difficult to draw any solid conclusions on this aspect of the behavior.
Figure 2.16 Susceptibility for a single crystal of gadolinium vs. temperature in four applied fields plotted against reduced temperature as described in the text.

Figure 2.17 Detail of high temperature peak in susceptibility for gadolinium. Numbers next to the curves indicate the applied field in kOe.
The possible temperature behavior of the peak near the Curie point is not the only puzzling piece of the Gd data. The other local moment systems studied show a sharp peak at $T_C$ with a rapid, almost zero temperature width drop in $\chi$ for $T < T_C$. Gd shows an increasing susceptibility with the supposed ferromagnetic transition peak sitting on this background. As was previously stated, the radio frequency data are consistent with published lower frequency susceptibility. It is possible that the impending spin reorientation is driven by a gradual change in one of the anisotropy constants, stiffening the magnetic structure over a broad temperature range.

2.3.6 GdPtIn

This is an hexagonal metal with a magnetic ordering temperature of 68 K. It carries a moment of 7.55 $\mu_B$ per Gd and the magnetic easy axis is parallel to the $c$-axis [Morosan et al. (2005)].

The measured susceptibility at 14 MHz for GdPtIn is presented in Fig. 2.18. The metallic nature of the material is evident from the background decrease in $\chi$ as temperature decreases. The measured $T_C$ is approximately 67.5 K which is consistent with the published value. Full suppression of the peak was not achieved as an applied field of 3 kOe resulted in the sample being pulled out of the frozen grease. The general behavior is still evident and consistent with the observed local moment behavior.

A second measurement at 28 MHz was made with the $^4$He systems allowing for a pullout, empty coil resonance to be determined. This permitted a determination of the absolute value of $\chi$. Results of that measurement are presented in Fig.2.19. It is noteworthy that even at $T_C$ the measured susceptibility is still skin depth limited implying the divergence of $\chi$ at the ordering temperature is likely suppressed by the finite frequency.

2.3.7 Ce$_3$Al$_{11}$

Ce$_3$Al$_{11}$ is a very good metal with ferromagnetic order setting in at 6.2 K. Upon further cooling, a transition to an incommensurate magnetic structure at 3.2 K [Boucherle et al.
Figure 2.18 Susceptibility vs. temperature for GdPtIn in different applied fields. *Inset:* Peak suppression (left axis, filled circles) and temperature shift (right axis, hollow squares) as a function of field.

(1995)]. There are two distinct cerium sites in the lattice. One carries a moment of 1.27 $\mu_B$ while the other is 0.24 $\mu_B$.

Both transitions are readily evident in the TDR data (Fig. 2.20). The para- to ferromagnetic transition is consistent with the other local moment systems studied (Fig. 2.21). The ferromagnetic to incommensurate transition shows a strong mean field behavior in zero field, with a sharp step in $\chi$ (Fig. 2.22).

To further explore these transitions, heat capacity measurements were taken vs. temperature in six dc fields on a larger sample. The dc field was aligned with the magnetic easy axis when the sample was in the ferromagnetic state. Figure 2.23 displays the results of these measurements. The applied field was varied from 0-1 kOe in steps of 0.2 kOe. The behavior of the anomaly associated with the ferromagnetic ordering at 6.2 K as the applied field is increased is consistent with what is seen in CeVSb$_3$. At first the low temperature feature looks very different from what is seen in susceptibility. There is a step-like change in $c_P$ at the transition, but a second transition not seen in the rf susceptibility data is evident. At first this is somewhat
Figure 2.19  28 MHz susceptibility for GdPtIn near $T_C$ in fields from 0-400 Oe in 100 Oe steps. Higher fields have lower amplitude maxima. *Inset:* Zero field susceptibility over entire measured temperature range.

Figure 2.20  $\chi$ vs. temperature for Ce$_3$Al$_{11}$ in applied fields from 0 to 500 Oe.
Figure 2.21 Detail of the para- to ferromagnetic phase transition in Ce$_3$Al$_{11}$.

Figure 2.22 Detail of the ferromagnetic to incommensurate structure in Ce$_3$Al$_{11}$.
confusing. However, these crystals were grown out a tin flux. The smaller sample used in the TDR measurements likely had no residual tin on its surface, thereby limiting the detection of the superconducting transition. Further, if there are tin inclusions in the sample then due to the excellent screening capabilities of Ce$_3$Al$_{11}$’s low resistivity, these inclusions would not be probed. Heat capacity does not suffer from this screening effect, and would detect included tin rather easily. If the second low temperature peak is ascribed to tin, then it is seen that the heat capacity suggests a mean field second order transition.

![Figure 2.23](image)

*Figure 2.23* Heat capacity for Ce$_3$Al$_{11}$ in six applied magnetic fields. Numbers indicate the extremes of applied magnetic field in kOe as described in the text. *Inset:* Detail of the low temperature transition for 0 and 1 kOe.

### 2.3.8 Fe$_{1/4}$TaS$_2$

The layered structure of the transition metal dichalcogenide TaS$_2$ permits the intercalation of other metal ions, nominally changing the formula to $M_x$TaS$_2$. $M$ is a 3$d$-transition metal and under certain circumstances long range magnetic order may occur. The details of the order depend rather strongly on the type and amount of intercalated ion, $x$. If $M=$Fe long range
magnetic order sets in for $0.2 \leq x \leq 0.34$ and for $x = 1/4$ or $1/3$ an ordered superlattice forms. Further, the ordering temperature is non-monotonic with doping concentration, reaching a maximum at approximately 150-160 K for $x = 1/4$ [Eibschütz et al. (1981)]. Band structure calculations on Fe intercalated at the concentration of $x = 1/3$ suggest a large imbalance between the two spin polarizations of the conduction electrons contributed by the iron [Dijkstra et al. (1989)] which may hint at a band component of the ferromagnetism. For the $x = 1/4$ concentration, however, the measured ratio of the paramagnetic to saturation moment is only slightly larger than 1 [Eibschütz et al. (1981)]. This suggests that this system is more likely localized than itinerant under the Rhodes-Wholfarth interpretation scheme [Rhodes and Wohlfarth (1963)].

Recent work on single crystals of Fe$_{1/4}$TaS$_2$ [Morosan et al. (2007), Checkelsky et al. (2008)] has shown extremely sharp switching fields in the $M - H$ loops and anomalous Hall effect and magnetoresistance associated with this sharp switching. The time dependence of the switching was studied by Morosan et al. (2007). There it was found that the switching speed increased nearly linearly with temperature in the range $5 \leq T \leq 18$ K. The time for magnetization reversal was on the order of 0.1-0.8 ms. The domain structure associated with such a sharp transition is assumed to show abrupt changes at the switching fields.

With this in mind, the domain structure of single crystal Fe$_{1/4}$TaS$_2$ was explored via magneto-optical (MO) visualization utilizing the Faraday rotation in an indicator. Further, the radio frequency magnetic susceptibility was measured at 28 MHz via a sensitive tunnel diode resonator (TDR) technique. The magneto-optic results show unusual low field domain behavior over time. RF susceptibility shows thermal hysteresis at approximately the same temperatures that domains are seen to form in MO data. Further, the local moment magnetic phase transition is evident in the TDR data. Single crystals of Fe$_{1/4}$TaS$_2$ were grown via iodine vapor transport and characterized as to quality as described by Morosan et al. (2007). Samples are platelets with the crystallographic $c$ axis perpendicular to the plane of the plate. This axis is also the magnetic easy axis in these materials. A smaller triangular specimen of area 0.67 mm$^2$ by 0.05 mm thick was chosen for the sample in this work.
Fig. 2.24 presents the zero field rf susceptibility of Fe$_{1/4}$TaS$_2$ in arbitrary units vs. temperature on sweeping up and down. The ferromagnetic transition is observed as a peak in $\chi$ at $T_C \approx 155$ K. Below $T_C$ the measured susceptibility drops in accordance with the resistivity decrease due to a loss of spin disorder scattering [Eibschütz et al. (1981)]. In the vicinity of 55 K there is an observed hysteresis characterized by breaks in the slope of $\chi$ vs. $T$. The inset shows the general effect of applied fields on the hysteresis. Runs performed in field were field cooled in the next lowest field and then $H$ was increased to the value for the run. To illustrate, the $\chi(T)$ data collected in an applied field of 500 Oe was field cooled in 400 Oe. At base temperature ($\sim 2$ K) the field was increased by 100 Oe at 10 Oe/s. A plot of $d\chi/dT$ vs. $T$, as shown in Fig. 2.25(b), allows for a precise determination of the maximum change in slope for both the warming and cooling curves which are taken to delimit the hysteresis region. In Fig. 2.25(a) hysteresis region is marked as a function of field. Horizontal dashed lines denote temperatures at which field scans were performed. Panel (c) shows the width of the hysteresis defined as the difference between the upper and lower temperatures from panel (a). First, for
low fields the hysteresis shifts to lower temperatures with a gradually decreasing width. At a critical field of approximately 700 Oe there is a dramatic increase in the low temperature boundary and a corresponding decrease in the width of the hysteresis. Thereafter, the width of the hysteresis grows slightly.

Figure 2.25  Breakdown of the hysteresis region in applied fields. Panel (a) presents the boundaries of the hysteresis vs. applied field. The dashed lines are temperatures at which field scans were taken. Panel (b) is the zero field \(d\chi/dT\) vs. \(T\) demonstrating how the boundaries in (a) were determined. Panel (c) is the width of the hysteresis as defined in the text.

Fig. 2.26 presents the field dependent data at three temperatures in and above the hysteresis region. In all curves the sample was zero field cooled, warmed to the measurement temperature and the field was swept up to +2.6 kOe, down to -2.6 kOe and back to zero. As a check on the polarity of the field, experiments were also run sweeping to negative field first. A slight zero field difference in \(\chi\) exists, most notably for the 54 K trace. However, this is likely due to a small temperature drift on the order of 0.4 K through a comparison of the zero field temperature swept data. \(\chi(T = 50K, H)\) data are below the zero field thermal hysteresis, but at a field of
Figure 2.26 $\chi$ vs. $H$ curves for three temperatures near the hysteresis region. The arbitrary units in this figure are the same as those in Fig. 2.24.
about 100 Oe it crosses the low temperature boundary. At \( T = 54 \) K the data begins in this hysteresis region, while at \( T = 64 \) K the sweep is done above it. From Fig 2.25(a) it is obvious that the lowest temperature field scan crossed the low temperature hysteresis boundary at 100 Oe. At about 650 and 1000 Oe it crossed the interpolated low temperature boundary twice more. In all three of these crossings the mid temperature scan \( (T = 54 \) K) did not cross any hysteresis boundary. However, the qualitative features in both of the lower temperature scans are similar. To better compare the three field scans Fig. 2.27 shows the change in \( \chi \) due to field taking the zero field susceptibility as a reference point. The high temperature field sweep may be understood in the context of polarizing spins. As the applied field increases there is an increasing preference for the spins to align with the field. The dynamic response of the moments in the sample decreases as a consequence and the rf susceptibility reflects this.

![Figure 2.27](image)

**Figure 2.27** \( \Delta \chi \) vs. \( H \) for the three field scans. **Inset:** Detail of the low field region.

Within the assumed domain formation region the effect of the field is to increase the relative fraction of domains parallel to the field at the expense of all others. The effect of the rf probe
field is to change the alignment of the spins by a small amount. In a dc bias field there is a preferred direction for the spins to point. Keeping in mind that the magnetic easy axis is aligned with the dc and rf fields, a spin residing in a domain parallel to the applied field will contribute a greater moment change in response to the rf field than one in an antiparallel domain. This can be seen by considering the thermal effects. In general a spin will not point exactly along (parallel or antiparallel) the line of applied field. Rather it will be tilted away at some angle due to thermal randomization. During the half cycle when the rf field is parallel with the applied field there will be a slightly greater tendency for all spins to point that direction. Those spins in domains whose magnetization points along the applied field will rotate more readily toward the field direction as this will minimize both the Zeeman and anisotropy energies. Spins in domains with antiparallel magnetizations will also tilt toward the applied field thereby reducing Zeeman energy. However, in this case there is an increase in anisotropy energy (Fig. 2.28). Therefore, the change in the bulk moment from these antiparallel domains is reduced compared with the parallel domains. On the other half of the rf cycle both parallel and antiparallel spins are working against the Zeeman energy from the bias field and there will not be as great a response in addition to the increase in anisotropy energy for the parallel domain moments. So as the fraction of sample in domains parallel to the applied field grows the measured \( \chi \) grows as well. At some point, the field has essentially saturated the sample and driven it into a single domain. Further increasing of the field increases the Zeeman energy effectively ‘freezing out’ the response of the spins.

The low field region of the 50 and 54 K scans shows a characteristic field of 100 Oe observed both upon increasing and decreasing the dc bias field. Below this field the susceptibility grows very rapidly at which point the change in \( \chi \) is much more gradual. In terms of the preceding argument, this rapidly increasing \( \chi \) would be in response to the weakly pinned or free domain walls. As mentioned previously, this frequency band is suitable for measuring domain wall resonance effects. It is possible that for this material 28 MHz is quite close to a normal vibrational frequency for domains, in which case at least some of the observed effects would be frequency dependent. The only way to be certain is to perform a careful study of the
Figure 2.28 Illustration of the parallel/antiparallel domain argument for field dependent magnetization.
susceptibility over a frequency window of $\pm 10$ MHz at the least.

2.3.9 $\text{Y}_2\text{Fe}_5\text{O}_{12}$

$\text{Y}_2\text{Fe}_5\text{O}_{12}$ (YIG) is a transparent, insulating ferrimagnet. Ferrimagnets are materials wherein the magnetic moments are arranged antiferromagnetically, however each of the two sublattices carry different moments per ion. Therefore, one of the lattices has a larger magnetization and the material as a whole carries a moment below the ordering temperature. YIG is used in our lab as a magneto-optical indicator to image magnetic induction profiles in different samples. The sample under consideration consists of a multi-layered structure of a mirror surface covered by a film of YIG which is further covered by a clear protective capping layer. It carries a moment at room temperature, and is well suited to serve as a sanity check for the response of the Inferno setup to verify the general nature of the local moment phase transition. The magnetic moment is in the plane of the film, and this plane was aligned with the rf field. Measured $T_C$ is 425 K from the Inferno (Fig. 2.29). As can be seen, strong local moment behavior, overwhelming the background signal from the copper sample holder is evident. Subtraction of the averaged background curves gives a narrow, well-defined peak. Just above $T_C$ there is a sharp drop in $\chi$ which may be due to the ferrimagnetic (over ferromagnetic) nature of the material. Or it may be due to the thin film geometry of the sample. A third possibility is that for YIG in this configuration 36 MHz is above some sort of critical frequency where the response of the material changes so that $\chi$ drops immediately prior to ordering. The precise origin of the effect is not as important as the fact that the peak is well defined and exceptionally well-localized in temperature. If the full amplitude is taken to be from maximum peak to minimum dip, the full width-half maximum value of the peak is only 5% of $T_C$. This narrowness is in keeping with other local moment behavior.
Figure 2.29  Measured susceptibility for a YIG thin film vs. temperature for different applied fields as noted by the magnet current. Inset: Temperature and amplitude of the peak as a function of magnet current. Curves are guides to the eye.
2.4 Evolution of $\chi(T)$ curves in applied field

Some common features are seen in all local moment systems. First, there exists a well-defined narrow peak at $T_C$ in zero applied field. This peak is suppressed in amplitude and shifted to higher temperatures as the applied field is increased. This peak is clearly associated with the phase transition. The behavior of $\chi(T)$ for Fe$_{1/4}$TaS$_2$ indicates that the peak seen at $T_C$ is unrelated to domains. Further indication of this stems from the magnetization versus field for CeAgSb$_2$. This compound is pushed into the single domain state by fields as small as 50 Oe, but the peak behavior persists up to several hundred oersted. Another argument against a domain response is the observed fact of a rapid increase in $\chi$ for $T > T_C$. In this temperature region, there are no domains because there is no long-range order.

This peak can be understood qualitatively by simple ferromagnetic exchange arguments. In zero applied dc field, the individual moments respond to the rf excitation field and a bulk moment is induced. The total moment of the sample is the thermal average of the atomic moments in the sample. As the temperature is lowered close to the Curie point, the exchange energy becomes competitive with thermal fluctuation energy, $k_B T$. Therefore, the individual moments begin to respond in clusters, the linear dimension of which is on the order of the correlation length. For a given applied field there is a proportionately larger positive magnetic response of the sample and a larger measured $\chi$. Upon crossing $T_C$ the exchange interaction dominates the response of the sample. The small rf field is unable to induce a change in the sample moment because such a response requires the rotation of spins away from mutual parallel alignment. In effect, the atomic moments are ‘frozen’ in place with respect to the tank coil’s ac field. This explains the rapid decrease in $\chi$ for temperatures just below $T_C$.

Application of a dc bias field introduces a Zeeman splitting on the moments, giving a preferred orientation parallel to the applied field. When the dc field direction coincides with the eventual ordering direction, it is easier for exchange interactions to overcome thermal randomization. So, the crossover that the maximum in $\chi$ marks can occur at a higher temperature. A second effect of this Zeeman splitting is to reduce the change in the sample moment induced by the rf field. This results in a reduced amplitude in $\chi$ as temperature is lowered.
Quantitative analysis of the phase transition generally lies in the realm of scaling theory, and it will be addressed later. However, Sznajd (2001) presents an argument that the temperature evolution of the peak in $\chi$ with applied field is not associated with critical fluctuations at all. It is also stated that within the Landau mean-field theory of second order phase transitions this temperature should depend on applied field as a power law. Under this argument, the predicted thermal evolution for the peak in $\chi$ is it grows as $h^2$ while for cubic (essentially isotropic exchange) it should grow like $h^{2/3}$. However, it seems that in his derivation, Sznajd made a sign error, so his conclusions are possibly not valid. Still, it does offer a starting point for attempting to derive some knowledge of system or the phase change.

If the effect of the dc bias field is assumed to simply add an ordering energy term to the exchange, then it would be expected that the shift in the temperature of the maximum would be linear in field. Returning to the mean field model, one obtains

$$M(T, H) = M_0 \frac{\mu(H_{ex} + H_{app})}{k_BT}.$$ (2.70)

From Eqs. 2.19 and 2.20, however, it is unclear how the applied magnetic field will quantitatively effect the magnetic susceptibility. Recourse to the Brillouin expression for magnetization (Eq. 2.8), allows the leading correction to the susceptibility to be determined. However, an ad hoc introduction of the ordering temperature is needed. In one sense, such an artificial introduction of a parameter seems unjustified. Still, it could be argued that Landau developed his theory with just such an assumption, i.e. it is an experimental fact that there is an ordering temperature. Boldly charging ahead the magnetization for the spin-1/2 case is

$$M(t, h) = M_0 \tanh \frac{\mu_B h}{k_B t}.$$ (2.71)

where $h = H_{app} + H_{int}$ is the sum of the applied field and the internal field from the moments, $t = T - T_C$, and $M_0 = -N g \mu_B J/V$ the susceptibility can be determined by differentiation. This gives

$$\chi(t, h) = \frac{\mu M_0}{k_B t} \left(1 - \tanh^2 \frac{\mu_B h}{k_B t}\right).$$ (2.72)
Generally one would expand the hyperbolic tangent for small arguments. The validity of such an expansion must be justified since near the ordering temperature $t \approx 0$. In the zero applied field case, this can be dealt with by noting that above $T_C$ the magnetization is zero (in the mean field theory). Application of a bias field forces the numerator to be finite. Concurrently the temperature of the maximum shifts higher so that $t$ is finite as well. Therefore it seems reasonable that the argument in the hyperbolic tangent will stay small. The expansion of $\chi$ leads to

$$
\chi(t, h) \approx \frac{\mu M_0}{k_B} \frac{t^3}{t^4 + (\mu_B h t/k_B)^2 + (\mu_B h/\sqrt{2k_B})^4}
$$

(2.73)

The temperature of the maximum in $\chi$ can be determined by taking the derivative with respect to $t$. This gives

$$
\frac{\partial \chi}{\partial t} = \frac{-at^6 + a(\mu_B h)^4 t^4 + (3a/4)(\mu_B h)^4 t^2}{(t^4 + (\mu_B h)^4)^2}
$$

(2.74)

where $a = \mu_B M_0 / k_B t$ and $b = \mu / k_B$. The condition for an extremum is met when the numerator is 0. Two of the six roots are 0, two are imaginary, and two are given by

$$
t = \pm \sqrt{-\frac{3\mu_B h}{2k_B}}.
$$

(2.75)

The positive root corresponds to the physically relevant situation. From such a simple argument, the shift in $t$ is expected to be linear in $h$, confirming the simple argument given above. What is gained is, for a spin-1/2 system, the slope of a plot of $t$ vs. $H_{app}$ should be $\sqrt{3/2} \mu_B / k_B$.

The temperature in Eq. 2.75 can be put back into Eq. 2.73 to get $\chi_{max}$ vs. $H_{app}$. Doing so gives

$$
\chi_{max} = \frac{3}{8} \sqrt{\frac{3 M_0}{2h}}
$$

(2.76)

and the expectation is that the maximum in susceptibility should be suppressed like $(H_{ex} + H_{app})^{-1}$.

To generalize this to arbitrary spin, it is easier to return to Eq. 2.8 and expand it for small arguments.

$$
M(t, h) \approx M_0 \left[ \frac{h y}{12 J^2 t} \left( (2J + 1)^2 - 1 \right) + \frac{y^3 h^3}{45 (2J)^4 t^3} \left( 1 - (2J + 1)^4 \right) \right]
$$

(2.77)
In the above $M_0$, $h$, and $t$ have the same meaning as in Eq. 2.71 and

$$y = \frac{g_J \mu_B J}{k_B}. \quad (2.78)$$

Differentiating with respect to $h$ results in

$$\chi(t, h) \approx M_0 \left[ \frac{y}{12J^2t} \left( (2J + 1)^2 - 1 \right) + \frac{y^3h^2}{15(2J)^4t^3} \left( 1 - (2J + 1)^4 \right) \right]. \quad (2.79)$$

The susceptibility has a maximum at the temperature

$$t = + \frac{g_J \mu_B h}{k_B} \sqrt{\frac{3 \left( 1 + (2J + 1)^2 \right)}{20}} \quad (2.80)$$

Again, the temperature of the maximum in $\chi$ is expected to shift linearly with applied field. On substituting $J = 1/2$, equation 2.80 reduces to 2.75 apart from a factor of $1/\sqrt{2}$. Substituting back into Eq. 2.79 gives

$$\chi_{\max}(h) \approx M_0 \frac{2J(J + 1)}{9h} \sqrt{\frac{10}{3(2J^2 + 2J + 1)}} \quad (2.81)$$
Figure 2.30  Temperature of the peak in $\chi$ with applied field for CeVSb$_3$ as measured along the c-axis. *Inset:* Log($\Delta T$) vs. Log($H$) with a linear fit to the high field. Fit range is indicated by the arrows in both the main graph and the inset.

Figure 2.31  Temperature of the peak in $\chi$
2.5 Anisotropy in CeVSb$_3$

When $\chi_{ac}$ is measured perpendicular to the magnetic easy axis, obvious differences in the data are seen (Fig. 2.32). First, the amplitude of the peak at $T_C$ is approximately 40 times smaller. Also the field required to suppress the peak to 10% of the zero field value is nearly 11 times larger for the perpendicular orientation (Fig. 2.34). Finally, the temperature of the maximum is only weakly dependent on the applied field (inset of Fig. 2.33).

![Figure 2.32](image)

**Figure 2.32** Comparison of zero field susceptibility for CeVSb$_3$ measured parallel and perpendicular to the magnetic easy axis.

The low temperature difference between the directions can be explained in two ways. First, the resistivity of this material along the c-axis is greater than along the b [Sefat et al. (2008)]. Since the rf field probes the resistivity perpendicular to it, when measuring $\chi_c$ $\rho_b$ is probed and vice versa. An alternative possibility is that when $\chi$ is measured perpendicular to the easy axis the rf field can tip the ordered moments coherently. While measuring $\chi$ parallel to the easy axis, the rf field is insufficient to flip the moments resulting in no change in magnetic moment. The deviation at higher temperatures is a direct result of the differing spin susceptibility, as the published resistivity along b is less than that along c. The screening in the ab plane (with the rf parallel to c axis) should be greater than the screening the in ac plane (rf parallel to b
axis) and measured $\chi$ should be less. This is not observed.

Figure 2.33  $\chi_{ac}$ measured perpendicular to the magnetic easy axis in different dc bias fields. The amplitude of the maximum is much less than that measured along the easy axis. The fields required for suppression are also considerably larger. Inset: Peak amplitude (left axis) and temperature of peak (right axis) versus applied field.

Fig. 2.33 shows $\chi$ vs. $T$ for CeVSb$_3$ measured along the b axis in different applied dc fields. Two features stand out when compared with the c axis data. First, the fields required to suppress the peak are much larger than the c axis case (6.5 kOe as compared to 0.5 kOe for a 90% suppression). Second, the temperature of the peak is basically unaffected by the application of the magnetic field, increasing less than 40 mK with an applied field of 5 kOe. This is in stark contrast to the c axis data where the maximum shifts up by almost 2 K with an applied field of 3 kOe. Both of these behaviors are summarized in Fig. 2.34.
2.6 Field Dependent Data on Local Moment Systems

The response of rf susceptibility to a swept field should be dominated by the changes in the spin susceptibility rather than the resistivity. This is true for low fields unless there is considerable magnetoresistance in the material. Data on Fe_{1/4}TaS_2 has been presented in Figs. 2.26 and deltachi. Domain wall motion was invoked to explain the initial increase in \( \chi \). Upon reaching a single domain state, the field is introducing an increasing Zeeman energy which reduces the response of the moments to the applied field. Field dependent data on three other materials (GdPtIn, CeAgSb_2, and CeVSb_3) is presented and discussed here.

Fig. 2.35 presents field dependent data in absolute units for GdPtIn at several temperatures. The magnetic easy axis was aligned with both the rf field and the dc field. Low temperature data shows an increasing \( \chi(H) \). At 21 K there emerges a maximum in \( \chi \) which is shifted to lower fields as the temperature increases. Above \( T_C \), in the fluctuating region, the susceptibility decreases monotonically with increasing field. In this figure, the zero field value of the susceptibility is equal to the value from the temperature swept data. To better
visualize what is happening to the spin susceptibility with applied field, $\Delta \chi$ vs. $H$ is shown in Fig. 2.36. In this figure, the zero field $\chi$ is set to zero and the changes that $H$ induces are shown. It is clear that the susceptibility is symmetric about $H = 0$ with the exception of a slight temperature drift in the 43 K run near 1.5 kOe. The lack of zero field hysteresis suggests that the rf field may encourage domain wall motion by shaking the walls out of defects which act as pinning sites.

![Graph](image)

**Figure 2.35** Field dependent $\chi$ for GdPtIn at the temperatures indicated next to each trace. $T_C \approx 68$ K for this material.

Fig. 2.37 presents the 3 K field swept data for CeAgSb$_2$. The virgin curve is shown in blue, and it shows a lower susceptibility. The field was swept from 0-2 kOe, where it was held for 15 minutes. Then the field was swept down to -2 kOe, back up to +2 kOe and finally back to zero. There is an initial decrease in $\chi$ for fields up to about 100 Oe. Thereafter the susceptibility increases in accordance with the domain wall argument previously presented. The dwell time at 2 kOe shows that the susceptibility relaxes with time. Upon lowering the field it is seen that, contrary to GdPtIn, the zero field susceptibility is somewhat higher after applying the field. At approximately -460 Oe there is a sharp increase in $\chi$ not seen in the initial field sweep.
Figure 2.36  $\Delta \chi$ vs. $H$ for GdPtIn for the temperatures indicated next to the curves.

On the return to +2 kOe this sharp feature again appears at approximately the same absolute field of 455 Oe.

Unpublished magneto-optic [Prozorov (2006)] studies suggest that there is a sharp domain switching at approximately 50 Oe in this material. If the sharp features seen in the rf data are due to this domain switching, it suggests that the presence of the field tends to stabilize the domains to much higher fields in this material. However, as this feature is not seen in the virgin curve it is difficult to say what might be happening there. Still, an interesting experiment would be to perform magneto-optical visualization on a sample in the presence of a rf field to determine what, if any, effect that oscillating field has on the domain structure.

This interpretation is in direct conflict with that for GdPtIn. As such, there must be an attempt to reconcile the differences. CeAgSb$_2$ is believed to have in plane antiferromagnetic order with a canting of the Ce moments which gives rise to the small ferromagnetic component along the c axis. For simple antiferromagnetic order, the susceptibility perpendicular to the ordering plane is expected to be larger than that measured in plane. Applying a magnetic field
Figure 2.37 3 K $\chi(H)$ data for CeAgSb$_2$. The sharp features seen at approximately ±450 Oe are ascribed to a rapid domain structure change.
should reduce the susceptibility by introducing a common tilt to all the spins, forcing them in one direction. As the field increases this tilt should increase and the dynamic response of the system should decrease. The canting of the spins in this sample is a result of an internal interaction giving rise to a spontaneous moment and ferromagnetic domains. In this case it is expected that the application of increasingly larger fields should affect the domains in a manner similar to that previously suggested. The complication arises from the effect of the in plane ordering. What remains in common with GdPtIn, CeAgSb$_2$, and Fe$_{1/4}$TaS$_2$ is that at base temperature the $\chi(H)$ curves show an initially increasing susceptibility for increasing field. For temperatures above $T_C$ there are considerable fluctuations in the atomic magnetic moment directions and application of field decreases them. The result is a decrease in $\chi$.

These results are to be contrasted with CeVSb$_3$. In the top panel of Fig. 2.38 the $\chi(H)$ curve for CeVSb$_3$ is presented. The virgin curve shows considerable difference when compared with the negative sweep. The bottom panel of Fig. 2.38 explains the differences. The temperature of the sample drifted by approximately 15 mK on the initial field sweep. This drift was sufficient to change the measured susceptibility via a change in resistivity. Irrespective of this temperature drift, there is a dramatic difference between the data on CeVSb$_3$ and the other local moment ferromagnets presented. Even though the sample is well into the ordered state ($T < 0.5T_C$) there is a pronounced decrease in $\chi$ as field increases. In absolute units this decrease is smaller than the change in CeAgSb$_2$, but the slope of the $\chi - H$ curve is negative in the vanadium compound. The negative slope is suggestive of a fluctuating component in the magnetism. Even though the sample shows strong local moment behavior, it is possible that the conduction band electrons are contributing to the dynamic response of the material. The field dependent response of itinerant ferromagnets is discussed in Ch. 4. Further, the heating effects of the rf field on various samples is explored in Ch. 6. There it is seen that in samples with considerable band magnetism components the rf field heats the material substantially more than in a magnetic insulator or a non-magnetic metal. All of this taken together suggests that while the magnetic moment in CeVSb$_3$ is localized on the cerium sites, there is a substantial enhancement of the conduction band polarizability.
Figure 2.38  Top $\chi(H)$ at approximately 2 K for CeVSb$_3$. Bottom Sample temperature vs. applied field for the same run.
2.7 Summary

The general features of radio–frequency magnetic susceptibility in local moment ferromagnets have been explored. The expected divergence in $\chi$ at $T_C$ manifests as a sharp peak in zero applied field. Application of a static field suppresses the peak and shifts it to higher temperatures when the rf–field and static field are parallel with the magnetic easy axis in the crystal. In the case where both fields are perpendicular to the magnetic easy axis, a peak is still observed. However, the zero field amplitude of this peak is greatly suppressed relative to measurements along the easy axis. Applying a static field for a hard axis orientation does not appreciably shift the temperature of the peak. The fields required to suppress the hard axis peak are much greater than those required to suppress the easy axis peak.

Constant temperature field dependent data show an initial increase in $\chi$ with increasing field for temperatures below $T_C$. For many samples studied there exists a small field above which $\chi$ begins to decrease. The physical origin for the observed maximum is unclear. The maximum in $\chi$ could be related to the elimination of domains. At higher temperatures the domain walls are much less likely to be pinned by defects in the sample. Therefore, it is easier to move the domain walls by applying a field. Once the sample is monodomain further increasing the field decreases the susceptibility. For temperatures above $T_C$, $\chi$ decreases monotonically with increasing field. This behavior is consistent with a paramagnet in an applied field.
CHAPTER 3. Failure of Critical Scaling Analysis of the Phase Transition

3.1 Introduction

The quality of the data collected by the TDR suggests that it may provide information regarding the physics governing the phase transition. This physics falls under the subject of critical scaling analysis. An overview of the theory of critical scaling is provided first. Following is application of this analysis to the systems CeVSb$_3$, CeAgSb$_2$, and YTiO$_3$. The failure of the TDR data to properly scale suggests that these data may lie on the boundary between the static and dynamic regimes.

Experimentally it is known that the behavior of the magnetization, heat capacity, and magnetic susceptibility near $T_C$ are dominated by power law dependencies in field and temperature. The various exponents assigned to each are

\[ C_P \sim \tau^{-\alpha} \]  
\[ m \sim \tau^{\beta} \]  
\[ m \sim h^{1/\delta} \]  
\[ \chi \sim \tau^{-\gamma} \]

The behavior of a system near a phase transition falls into the category of critical point analysis. The value of the particular thermodynamic variable driving the transition that sits on the boundary between the ordered and disordered phases is the critical point. Often this variable is temperature, but it may be field or pressure as well. The latter two may fall under the category of quantum phase transitions which differ from classical phase transitions in that it
is quantum fluctuations that drive the change of phase. In a classical phase transition thermal fluctuations are responsible for the phase change. The basic idea behind critical point analysis is that at the critical point the system has no intrinsic length scale over which correlations are established.

From a ferromagnetic standpoint, when the temperature is much higher than the Curie temperature the system is completely disordered and thermal fluctuations disrupt even nearest neighbor correlations. As the temperature decreases the ferromagnetic exchange interaction tends to align neighboring spins with one another. However, for any given spin there is a characteristic length, $\xi$, beyond which two spins are uncorrelated. This means that if a spin at point $\mathbf{r}$ points in some direction, then spins less than $\xi$ away from $\mathbf{r}$ in some sense will tend to point in that same direction. Conversely, spins farther than $\xi$ will not have any tendency to point in the same direction as the spin at $\mathbf{r}$. The closer $T$ is to $T_C$, the greater $\xi$ is, until at $T_C$ where $\xi$ diverges. The divergence of $\xi$ implies that there is no characteristic length in the problem. Therefore the free energy and its derivatives (magnetization, heat capacity, magnetic susceptibility, etc.) may be rescaled in some way provided the thermodynamic variables (field and temperature) are suitably scaled as well. Authoritative reviews of the subject are provided by Kadanoff et al. (1967) and Fisher (1967). Stanley (1999) offers a colloquial introduction to the concepts associated with these critical phenomena. Three basic ideas fall out of critical scaling theory. The first is the existence of relationships between the various exponents describing the behavior of the system as it approaches the phase transition. These are called scaling laws. The second idea is that of data collapse. This finds that data collected on, say, magnetization vs. temperature in various fields, should all fall onto a single pair of curves that approach one another as $T \to T_C$ if the data are plotted appropriately. The proper way to plot susceptibility data will be extracted below.

A third, separate concept of scaling is that of universality [Stanley (1999)]. This is the observed fact that generally magnetically ordered materials fall into different classes based on the nature and dimensionality of the ordering. Each class has its own set of critical exponents (Table 3.1). For ferromagnets it is interesting that while there are widely varying values for $\beta$
and $\delta$, the product of the two (which is the relevant quantity for scaling susceptibility data) is always close to 1.5.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>2-D Ising</th>
<th>3-D Ising</th>
<th>3-D Heisenberg</th>
<th>mean field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>0.12</td>
<td>0.31</td>
<td>0.31</td>
<td>0.5</td>
</tr>
<tr>
<td>$\delta$</td>
<td>15</td>
<td>5.0</td>
<td>5.2</td>
<td>3</td>
</tr>
<tr>
<td>$\beta\delta$</td>
<td>1.8</td>
<td>1.55</td>
<td>1.61</td>
<td>1.5</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.75</td>
<td>1.25</td>
<td>1.33</td>
<td>1</td>
</tr>
</tbody>
</table>

The free energy can be expressed as some unknown function of reduced temperature ($\tau = |T - T_C|/T_C$) and field ($h = \mu H/k_B T_C$) where $T_C$ is the suitably defined zero field transition temperature.

$$F = F(\tau, h)$$

(3.5)

$T_C$ is taken as the temperature of the maximum in $\chi$ as measured in zero field by the TDR. Under the scaling hypothesis if $F$ is multiplied by an arbitrary factor then the function is unchanged provided the arguments are multiplied by the same factor to some power.

$$\lambda^D F(\tau, h) = F(\lambda^a \tau, \lambda^b h).$$

(3.6)

The power $D$ on the prefactor reflects the fact that the free energy scales with the volume of the sample. Since the factor $\lambda$ is arbitrary, it may be chosen for computational convenience. Taking $\lambda^a \tau = 1$ implies $\lambda = \tau^{-1/a}$. This allows a substitution into the free energy, recasting it as

$$F(\tau, h) = \tau^{D/a} F(1, \tau^{-b/a} h).$$

(3.7)

From here, the temperature dependence of the zero field heat capacity can be determined.

$$C_P = \frac{\partial^2 F}{\partial \tau^2} \sim \tau^{D/a - 2}.$$  

(3.8)

Examining the relationship from Eq. 3.1 shows that $\alpha = 2 - D/a$. This is the first scaling law, and it relates the divergence of the heat capacity directly to the dimensionality of the system.
The exponent $a$ is, as yet, undetermined. However, further work can be done to determine how the magnetization and susceptibility depend on temperature and field. This will allow for an elimination of $a$ and $b$ in favor of $\alpha$, $\beta$, $\delta$, and $\gamma$.

Eq. 3.7 can be differentiated once with respect to field to determine the temperature dependence of magnetization. Doing so gives

$$m \sim \tau^{(D-b)/a}$$

(3.9)

in the limit of zero field. Combining this result with Eq. 3.2 and the relationship between $\alpha$, $D$, and $a$ just found gives $\beta = 2 - \alpha - b/a$. Returning to Eq. 3.6 the choice $\lambda^b h = 1$ can be made. In this case the free energy is recast as

$$F(\tau, h) = h^{D/b}F(h^{-a/b}\tau, 1).$$

(3.10)

Now, at the critical point ($\tau = 0$) the magnetization depends on field as

$$m \sim h^{D/b-1}.$$  \hspace{1cm} (3.11)

Again, comparison with the assigned labels for the critical indices shows that $\delta = b/(D - b)$. The free energy in Eq. 3.7 can be twice differentiated with respect to field to obtain the temperature dependence of the susceptibility. This gives

$$\chi \sim \tau^{(D-2b)/a}$$

(3.12)

which shows that $\gamma = (2b - D)/a$. Using the relationships between $D$, $b$, $a$, $\beta$, and $\delta$ it is possible to rewrite Eq. 3.7 removing reference to the exponents $b$ and $a$. Since $\beta = (D - b)/a$ and $\delta = b/(D - b)$ the product $\beta \delta$ is just $b/a$. This is the exponent on the reduced temperature in Eq. 3.7 (with a minus sign). Therefore, this form of the free energy may be rewritten as

$$F(\tau, h) = \tau^{D/a}F(1, h/\tau^{\beta \delta}).$$

(3.13)
Taking derivatives will alter the functional form of \( F \), but it will not change the argument of that function. All changes are taken into account by moving them to the prefactor. What this implies is that the relation 3.12 may be rewritten as

\[
\chi(\tau, h) = \tau^{-\gamma} G \left( \frac{h}{\tau^\beta \delta} \right). \tag{3.14}
\]

Moving the factor \( \tau^{-\gamma} \) to the left hand side shows that \( \chi \tau^\gamma \) is a universal function of \( h/\tau^\beta \delta \). If temperature dependent susceptibility data is collected in different fields, then a plots of \( \chi \tau^\gamma \) vs. \( h/\tau^\beta \delta \) should fall onto a single curve as the critical point is approached. This is termed ‘collapse of the data.’

### 3.2 Experimentally Determining Scaling Exponents

Ho et al. (1981) have presented a method of determining the scaling exponents \( \beta \) and \( \delta \) from measurements of the ac susceptibility in ferromagnets. The basis of their procedure is the simple fact that the derivative of a function is zero at a maximum of that function. They further exploit the idea that the derivative of a generalized homogeneous function is itself a generalized homogeneous function. \( \gamma \) can be determined from a log-log plot of the zero field susceptibility versus \( T - T_C \) on the paramagnetic side.

For a fixed field, the susceptibility goes through a maximum at some temperature, \( \tau_m \) near \( \tau = 0 \). At this temperature the derivative of the susceptibility with respect to temperature is zero, \( d\chi/d\tau = 0 \). This implies that \( G \) in Eq. 3.14 is independent of \( \tau \) at the maximum which is satisfied if its argument is constant, i.e. \( h/\tau^\beta \delta = \text{const} \). This leads to the conclusions that

\[
\tau_m \sim h^{1/(\beta \delta)} \tag{3.15}
\]

and

\[
\chi_m(h, \tau_m) \sim h^{(1/\delta) - 1}. \tag{3.16}
\]

The Widom relation can be exploited to rewrite the exponent on \( \tau_m \) as \( 1/\beta \delta = 1/(\gamma + \beta) \).
Therefore, it should be possible to determine $\gamma$, $\delta$, and the product $\beta \delta$ if $\chi_m$ and $\tau_m$ are plotted vs. $H$ on log-log axes. These should be straight lines whose slopes are the exponents.

### 3.3 Critical Scaling in CeAgSb$_2$ and CeVSB$_3$

The scaling analysis developed in earlier sections is not applicable to all of the systems studied. Ce$_3$Al$_{11}$ has two distinct cerium moments, and the assumptions going into the analysis of critical phenomena is that each magnetic site carries the same moment. Therefore, scaling in Ce$_3$Al$_{11}$ is not expected to work. Further, some samples (Gd, YIG, Fe$_{1/4}$TaS$_2$, and Pr$_2$Fe$_{14}$B) had obstacles to experimentally testing the critical phenomena. In the main, these problems were in the Curie temperatures of the samples. These temperatures were particularly difficult to reach without the addition of a considerable background signal and thermal lag. What this leaves for analysis are CeVSB$_3$, CeAgSb$_2$, YTiO$_3$ and GdPtIn. In this section, CeAgSb$_2$ and CeVSB$_3$ are studied. The next section addresses YTiO$_3$. As there was never a field sufficient to suppress the maximum in $\chi$ fully for GdPtIn, this data is not scaled. However, certain analyses regarding the peak is attempted.

To account for the resistive background coming from the metallic samples, a high field temperature sweep is subtracted from the lower field runs. The chosen field is sufficiently large to completely suppress the peak at $T_C$. As an example of the results of this process the difference between the lower field data in CeAgSb$_2$ and a 1 kOe run is presented in the main plot of Fig. 3.1. The inset shows the raw $\chi$ vs. $T$ for this same data.

In the course of examining the data from the various local moment systems, it was noticed that the peak amplitude associated with the phase change was suppressed as $H^{-1}$. However, a plot of $\chi_{max}$ vs. $H^{-1}$ deviates from linear for the lowest fields (see Fig. 3.2). This suggests that the true functional form is not $\chi_{max} \propto H^{-1}$, but rather that it is proportional to $(H + H^*)^{-1}$. Indeed, a plot of $\chi_{max}^{-1}$ vs. $H$ is linear. $H^*$ is the effective applied field in which the magnetic susceptibility diverges for the sample. The general behavior of the susceptibility maximum with applied field has been observed before in many ferromagnetic systems. Further, Kunkel et al. (1988) have predicted similar behavior for paramagnetic systems with no interaction for
Figure 3.1 Difference in $\chi$ vs. $T$ relative to a 1 kOe run for CeAgSb$_2$. Inset: Absolute $\chi$ vs. $T$ for data in the main panel.

$T \to 0$. In that work it is stated that such behavior from paramagnets provides evidence that the maximum is related to the static rather than the dynamic response of the system. This suggests that the systems are still in the static regime. However, if a comparison is made of similar measurements at different frequencies (14 and 28 MHz) it is seen that there are some differences in some of the samples [Vannette et al. (2008c)].

Figure 3.3 shows plots of the inverse peak amplitude against applied magnetic field. Both compounds show a linear relationship with a negative $H$ intercept, which is labeled $H^*$. This characteristic field represents the field at which the magnetic susceptibility would truly diverge. The linear relationship is also troubling for scaling analysis because it implies

$$\chi_m \sim h^{-1}.$$  \hfill (3.17)

In conjunction with Eq. 3.16 this suggests $1/\delta$ is zero and the value of $\delta$ is undefined. The absolute values of $H^*$ for the two compounds are reasonably close. Comparison of $H^*$ with
Figure 3.2  Peak amplitude (solid symbols, left axis) and inverse peak amplitude (hollow symbols, right axis) vs. applied field for YTiO$_3$.

Figure 3.3  (Color online) Inverse peak amplitude vs. applied magnetic field for CeAgSb$_2$ (a) and CeVSb$_3$ (b). Solid circles are data and the line is a linear fit. The $H$ axis intercept ($H^*$) corresponds to the applied field at which the susceptibility would diverge.
the fields required to suppress the susceptibility maximum, however, indicates a significant difference. For CeAgSb$_2$ $H^*$ is not quite a full order of magnitude below the suppression field. On the other hand, for CeVSb$_3$ $H^*$ is nearly a factor of 100 smaller than the suppression fields.

![Figure 3.4](image)

Figure 3.4  (Color online) Scaled plots for CeAgSb$_2$ in the paramagnetic state neglecting $H^*$ (a) and adding $H^*$ to all applied fields (b). As $T \rightarrow T_C$, the plot extends off to right. Both plots use the same exponents.

Scaling was attempted for CeAgSb$_2$. $\gamma$ was estimated from a double log plot of the zero field susceptibility while the product $\beta\delta$ was treated as an adjustable parameter. Using values of the applied field without modification failed to produce any reasonable collapse of the data (Fig. 3.4(a)). However, if $H^*$ determined from the plot of inverse peak amplitude versus applied field is added to all applied fields the resultant collapse is much better (Fig. 3.4(b)). In order to determine the relative quality of the data collapse, $\chi^2$ analysis was performed on data collected in the largest and smallest applied fields.

In comparing the two data sets it was seen that there was not a point by point match of the $x$ values in the data. To combat the data from the smallest field was parsed into seven point subsets, a midpoint and three points above and below the midpoint. Every point considered in
the $\chi^2$ analysis was treated as a separate midpoint. A fourth order polynomial was fit to each subset and the resulting fit parameters were used to interpolate the data so that a comparison between the largest and smallest field data could be made. Tests of this procedure on two identical cosine functions extending over 3 full periods, where $\chi^2 = 1$, resulted in $\chi^2 \approx 2.5$. By reducing the test data sets to half period lengths the procedure reduced the $\chi^2$ to 1.2. This lower value of $\chi^2$ on a monotonic curve was taken as the ideal. Typical $\chi^2$ values for the comparison of scaled data ranged from $>10^5$ to $<2$.

![Figure 3.5](image)

Figure 3.5 (Color online) Scaled plots for CeVSB$_3$ neglecting $H^*$ (a) and adding $H^*$ to all applied fields (b). Both plots use the same exponents.

Figure 3.5 displays scaled plots for the CeVSB$_3$ data. As with CeAgSb$_2$, $\gamma$ was estimated from a double log plot of the zero field susceptibility and $\beta\delta$ was treated as an adjustable parameter. In panel (a) $H^*$ is neglected while in panel (b) $H^*$ is added to all field values. Interestingly, for this sample the collapse of the data is somewhat better without considering $H^*$, however in both situations the collapse is very good.

The precise interpretation of $H^*$ is difficult. At first, one might think of it as the demagnetizing field. This view has the problem that the demagnetizing field is proportional to
the magnetization of the sample. Therefore, it should be recalculated for each applied field instead of being a single value. On the other hand, if this field is associated with the internal dipole field from the surrounding magnetic moments a separate complication is met. Using published values for structure and lattice parameters for CeVSb₃ [Sefat et al. (2008)] one can calculate the dipole field on one Ce ion from its neighbors. This is of the order of -800 Oe if one assumes a fully ordered lattice of 1.4 $\mu_B$ ions. It can be argued that near $T_C$, where the data is collected, the lattice is not fully ordered, so such a calculation is invalid. Indeed, at $T_C$ the magnetization is formally zero and therefore the dipolar field should be zero. There exists the possibility that this field is somehow related to the imagined Weiss molecular field that leads to ordering in magnetic samples. Again, there is a problem in that the Weiss field is little more than an imaginary mechanism as its magnitude should be several orders larger than what is presented here. However, $H^*$ represents the field that must be applied to result in true divergence in $\chi$. Therefore, it can be considered as opposing some other field in the sample. Taking this stance suggests that $H^*$ could be related to the exchange field leading to the magnetic order. Yet another interpretation is to consider $H^*$ as an effective field originating with the finite frequency of the measurement. In this case, it would be expected that for fields less than $|H^*|$ the response would be frequency dominated and the linearity of the inverse peak amplitude would be more strictly adhered to. For larger fields it, the suppression should then evolve sublinearly in accordance with the exponent $\beta\delta$.

Two different frequencies were used to determine if this last idea is the case in CeAgSb₂ and CeVSb₃. The previously reported data was taken at 14 MHz. Fig. 3.6 shows the inverse of the peak in $\chi$ vs. applied field for CeVSb₃ as measured at 28 MHz. It is seen that $H^*$ increases very slightly, but is the same as the 14 MHz data within the uncertainty. This notwithstanding, the observed linearity in the data points is striking, suggesting that the rf field is still in the dc limit, if frequency effects are to be invoked. The 28 MHz data was collected on a cube shaped sample approximately 1 mm on edge. The demagnetization factor would be smaller for this sample than for the thinner piece used in the lower frequency measurement.

Similar data collected at 28 MHz on a larger sample CeAgSb₂ with nearly the same aspect
ratio as the smaller sample suggests that this material is not in the static regime, as the measured $H^*$ is approximately 50% larger when compared to the 14 MHz data (Fig. 3.7). This interpretation is in keeping with the previous observation that scaling in CeAgSb$_2$ could only be accomplished by considering the effect of this characteristic field. However, the puzzling fact that the inverse peak amplitude is linear in $H$ up to 3 times $H^*$ tends to suggest that this may not be the case. A possible explanation is that there are multiple terms (Weiss ordering field, frequency, and geometric) all combined to give the effective $H^*$. It would be expected that the Weiss term is constant across samples as this is an intrinsic quality. Given the similarities of the shapes and aspect ratios of the samples, it is expected that the demagnetization effects would be the same. This leaves the main culprit as the frequency for inducing a change in $H^*$.

Similar analysis performed on a single sample of GdPtIn at both 14 and 28 MHz also shows that there is a different characteristic field for each frequency here as well. If $|H^*| \mu_{sat}/\mu_B$ is plotted against $T_C$ for several local moment samples, there appears to be a strong correlation (Fig. 3.8) that depends on measurement frequency. This lends some credibility to the idea that $H^*$ is tied to the exchange field, as there is a correlation between the magnetic energy...
associated with this characteristic field and the onset of long-range magnetic order. The higher frequency trend is very nearly linear while the lower frequency has some positive curvature for the samples studied. The YTiO$_3$ data at 14 MHz is considerably suppressed relative to the line joining CeAgSb$_2$ and GdPtIn at the same frequency.

Table 3.2 Characteristic fields from the analysis of peak amplitude with applied field.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_{sat}$</th>
<th>$T_C$</th>
<th>14 MHz $H^*$</th>
<th>28 MHz $H^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeVSb$_3$</td>
<td>1.4/Ce</td>
<td>4.5</td>
<td>-13</td>
<td>-16</td>
</tr>
<tr>
<td>CeAgSb$_2$</td>
<td>0.37/Ce</td>
<td>9.8</td>
<td>-45</td>
<td>-65</td>
</tr>
<tr>
<td>YTiO$_3$</td>
<td>0.85/Ti</td>
<td>23.7</td>
<td>-189</td>
<td>-676</td>
</tr>
<tr>
<td>GdPtIn</td>
<td>7.55/Gd</td>
<td>68</td>
<td>-187</td>
<td>-321</td>
</tr>
</tbody>
</table>
Figure 3.8 Plot of $H^* \mu_{sat}/\mu_B$ versus $T_C$ for the magnets studied in this work. There is an obvious correlation between the energy associated with $H^*$ and the Curie temperature. This suggests that $H^*$ is related to the ordering mechanism in local moment ferromagnets. Dashed lines are guides to the eye.

### 3.4 Scaling an Insulating Ferromagnet

Since it appears that scaling works best when the $H^*$ field is taken into consideration, presented scaled data on YTiO$_3$ immediately considers the effects of this field. Figs. 3.9-3.12 present the results of scaling in YTiO$_3$ under the exponents derived in the different models presented in Table 3.1. In all figures the lines marked ‘5%’ and ‘10%’ denote that fractional change in temperature from $T_C$. Since critical scaling is only valid close to $T_C$ it is natural to expect the collapse of the data to be better as $T \to T_C$. Indeed this is the case for all models. ($T_C$ is at $+\infty$ on the horizontal axis.)

The ‘best’ exponents for the scaling are taken to be those that result in a tighter collapse of the data farther from $T_C$ as determined via the previously discussed $\chi^2$ analysis. From the figures it appears that YTiO$_3$ falls into the 2-D Ising class of magnets. Caution must be exercised at this point, though, as the larger value of $\beta\delta$ in this model will stretch the horizontal axis considerably. This said, and considering the nature of the order giving rise to
Figure 3.9  Mean field scaling for YTiO$_3$.

Figure 3.10  2-D Ising scaling for YTiO$_3$. 
Figure 3.11 3-D Ising scaling for YTiO$_3$.

Figure 3.12 3-D Heisenberg scaling for YTiO$_3$. 
the ferromagnetic component (canted antiferromagnetism), there is little difference between the 3-D Ising and 3-D Heisenberg models.

An important aspect to note is that regardless of the values of the critical exponents, the gross features of the scaled data in YTiO$_3$ are expected for properly analyzed data. This material is an insulator which means the TDR measurement is only affected by the spin susceptibility. There is no resistive component to the data. Therefore, any modifications to the analysis, particularly as pertains to the handling of the skin depth component in the following section, will be judged based on how the resulting data compares with the YTiO$_3$ results.

### 3.5 Effect of Skin Depth Limit

Based on the analysis in Ch. 1, in the vicinity of a ferromagnetic phase transition, it is expected that the measured susceptibility be related to the magnetic permeability via Eq. 1.18

$$1 + 4\pi \chi = \sqrt{\mu}. \quad (3.18)$$

This neglects the contribution of the resistivity to the measured susceptibility. If this part is considered, from the previous analysis it is expected that Eq. 3.18 be modified so that

$$1 + 4\pi \chi = \sqrt{\mu \rho}. \quad (3.18)$$

If this is correct, then in skin depth limited samples true scaling should be attempted for $\mu$ instead of the measured $\chi$. In some sense this is more reasonable as the critical scaling is supposed to be performed on materials using the internal field rather than the applied field. The definition of $\mu$ is $dB/dH$ where $B$ is the magnetic induction. In the sample, this amounts to the actual field present due to all effects. However, previously demagnetization was not considered. Ignoring demagnetization is justified based on the observed fact that the susceptibility does not show a saturation effect at $T \to T_C$. If such geometric/finite size effects were considerable, then the zero field $\chi$ would show a plateau near the Curie temperature. In fact, the peak in $\chi$ is extremely narrow and very sharp for all local moment systems studied. This tends to suggest the effects of demagnetization are not so important here.
Any dramatic deviations from the nature of Figs. 3.9-3.12 in the scaled data will be taken as indication that the consideration of the skin effect near $T_C$ is not necessarily correct as previously derived. It is clear that for non-magnetic metals that the measured susceptibility does indeed recreate the effect of resistivity, as was shown for copper (Fig. 1.5). It is also shown later that field saturation of the spin response leads to a reproduction of the behavior of the resistivity (Fig. 4.6). What remains in doubt is how the mixing of $\mu$ and $\rho$ actually affect the data when $\chi$ formally diverges.

CeAgSb$_2$ is taken as the system under consideration here. The resistivity is low, so the sample is skin depth limited both above and below $T_C$. Further, the application of fields on the order of 1 kOe is sufficient to suppress the peak in $\chi$ at the transition. The previous scaling (Fig. 3.4) was accomplished by a simple subtraction of a 1 kOe run from the low field data sets. In what follows, a different method is used to attempt to account for the resistivity background.

Figure 3.13 presents the quantity $(1 + 4\pi\chi)^2$ vs. $T$ for CeAgSb$_2$ as measured at 28 MHz in several applied fields. If the analysis of the skin depth limited regime is correct, then these curves represent the quantity $\mu\rho$. The inset to Fig. 3.13 is a detail of the ferromagnetic ordering. Qualitatively these curves are very similar to the as measured $\chi$ vs. $T$ curves shown in Figs. 2.11 and 2.12. The main difference here is that the measured quantities are all positive.

Under the assumptions that (1) Fig. 3.13 accurately represents the combination of magnetic spin and electrically resistive components, and (2) the application of a 1 kOe field does not dramatically alter the resistivity but suppresses the magnetic contribution, dividing the lower field data sets by the 1 kOe run should result in $\mu$ vs. $T$ curves. Such curves are plotted in Fig. 3.14. It is evident that this is assumed to be the relative permeability.

The analysis developed by Ho et al. (1981) is applied to the determined $\mu$. Fig. 3.15 is a plot of $\log(\mu_{\text{peak}})$ vs. $\log(H)$ from 40-200 Oe. The data (with the exception of the 200 Oe point) all fall very close to a single line with slope -0.0248. This translates to a $\delta$ of 1.025. In some sense this is an improvement over the previous analysis where $\delta \to \infty$. The issue, though, is that the previous behavior of $\delta$ was observed in YTiO$_3$ as well. Further, the value
Figure 3.13 $\mu p$ vs. $T$ for CeAgSb$_2$ as determined by $(1 + 4\pi \chi)^2$. *Inset:* Detail near $T_c$.

Figure 3.14 $\mu$ vs. $T$ for CeAgSb$_2$ as determined by the method described in the text. *Inset:* Detail near $T_c$. 
of 1.025 is much too small for any model, mean field giving the smallest at $\delta = 3$. Failure to provide an appropriate value of $\delta$ does not preclude the possibility of scaling, though. As such, scaling was attempted for the $\mu$ data in CeAgSb$_2$. The results of the 3-D Heisenberg scaling are presented in Fig. 3.16 for three different fields. As there is no characteristic field derivable from this data, no field correction like what was done in Sec. 3.3 can be attempted.

![Figure 3.15](image)

Figure 3.15 Log($\mu_{peak}$) vs. log($H$) from the data presented in Fig. 3.14.

It is evident that the compensation of $\rho$ results in better collapse of the data. However, the fact that both above and below $T_C$ data follow precisely the same curve for a given field is troubling. In YTiO$_3$ the data above $T_C$ curved down as temperature increased while the data below $T_C$ curved up as temperature decreased. While the collapse of the data is quite nice with this method, it is unclear that the actual handling of the resistive component is better considering that the behavior of the scaled data far from $T_C$ is dramatically different from the insulating compound.

It can be argued that since what was scaled was the relative permeability, while the scaling hypothesis deals with the susceptibility, the failure of the data to scale is due to a subtle
Figure 3.16 3-D Heisenberg scaling for $\mu$ data in CeAgSb$_2$. Solid symbols are for data with the resistivity contribution accounted for, while open symbols present data where $\rho$ is still included.
mishandling of the analysis. It is apparent that the as derived \( \mu \) (with \( \rho \) compensated for by division) is in SI units with the assumption that the 1 kOe run has the same ac spin susceptibility as vacuum. In principle this should be equivalent to the assumption that subtracting the high field data set from the lower fields adequately compensates for the resistivity while not affecting the spin susceptibility. If this is indeed the case, then it should be possible to convert the extracted permeability to susceptibility. The relation between \( \mu \) and \( \chi \) in SI units is \( \chi = \mu - 1 \). Taking this tack and converting \( \mu \) to \( \chi \) does change the results of critical scaling analysis (Fig. 3.17. However, that change amounts to reflecting the scaled \( \mu \) data about the \( x \)-axis. Again the difference between these results and the insulating YTiO\(_3\) is obvious and taken as evidence that this is not the correct way to handle the resistive contribution to the measured \( \chi \).

![Figure 3.17 Scaled \( \chi \) data for CeAgSb\(_2\) after accounting for the resistive component.](image-url)
3.6 Summary

The radio–frequency data collected via the TDR does not adhere to critical scaling analysis. Various attempts to account for the resistive component in metallic ferromagnets fail to produce scaled data that approximates the insulating YTiO₃ with the exception of a simple subtraction of measured χ vs. T data in fields large enough to suppress the peak associated with the phase transition. This suggests that the simple subtraction method is the most suitable way of dealing with the resistive component of the measured χ. Analysis of the peak in χ near T_C extracts a characteristic field H*, the value of which depends on the measurement frequency. The frequency dependence of H* implies that it may in fact be frequency taking on the roll of an applied field in suppressing the peak in χ at the phase transition. If this were the case then for fields larger than H* a plot of 1/χ_{max} vs. H_{app} should take on a curvature appropriate to the value of the critical exponent δ. That this is not observed suggests that if the finite frequency is acting as a field, then this frequency band may lie on the boundary between the static and dynamic regimes.
CHAPTER 4. Itinerant Ferromagnets

4.1 Introduction

In comparison with local moment systems, itinerant ferromagnets carry their magnetization in the conduction band electrons. The fractional Bohr magneton moment of Ni and the discovery of ferromagnetism in ZrZn$_2$ [Matthias and Bozorth (1958)], of which neither constituent element displays magnetism, pushed the development of the theory of band ferromagnets.

Figure 4.1 compares temperature dependent dc susceptibility for the local moment CeAgSb$_2$ with that for the itinerant ZrZn$_2$ as measured in a Quantum Design MPMS-5. Two different techniques were used to determine these susceptibilities. Panel (a) shows the usual $\chi_{dc}$ where the magnetic moment is measured in a small applied field ($H = 20$ Oe) and $M/H$ is calculated. While this method is appropriate for temperatures well above $T_C$ where magnetization is linearly dependent on field over a fairly large field range, it should be expected to fail in the ferromagnetic state because $M$ is not necessarily linear in $H$ all the way down to $H = 0$. Bearing this in mind, a delta measurement of $\chi_{dc}$ was performed (results in panel (b)) as follows. Magnetic moment versus temperature was measured first in a 17 Oe field and then in a 22 Oe field. The difference in the resulting moment was divided by the 5 Oe difference in applied fields to determine $\Delta M/\Delta H$. The advantage of this method is that it only requires approximate linearity in $M(H)$ over the 5 Oe window defined by the upper and lower fields. Thus, it can be expected to approximate $\chi = \frac{dM}{dH}$ more closely. Obviously, a smaller $H$ window is more likely to conform to the linear $M(H)$ approximation.

While the delta measurement results in a lower susceptibility in both samples, both dc techniques produce very similar $\chi(T)$ curves. This is to be contrasted with the results of zero field radio frequency susceptibility versus temperature as shown in Fig. 4.2. Whereas the local
Figure 4.1 Comparison of various dc measurements of magnetic susceptibility of CeAgSb$_2$ with ZrZn$_2$. Static measurements do little to differentiate between the two types of ferromagnets.
moment system shows a sharp, well defined peak in $\chi_{ac}$ at the Curie temperature, the itinerant system exhibits a broad maximum well below $T_C$.

![Graph](image1)

![Graph](image2)

Figure 4.2 Comparison of the ac susceptibility of local moment CeAgSb$_2$ with itinerant ZrZn$_2$ in zero applied field. As was discussed in Chapter 2, the peak at $T_C$ in CeAgSb$_2$ is associated with the critical fluctuations driven by the phase transition. The stark difference between the local and the itinerant response was the driving force behind this chapter.

As local moment systems have their magnetic moments closely associated with particular ions in the lattice, it seems reasonable to assume these moments would have access to lattice vibrations, or phonons, as a method of dissipating energy. Conversely, in itinerant magnets
the conduction band electrons are free to wander about the lattice, and therefore might be expected to interact less strongly with phonons. This may be important in this work because the spin-lattice interaction time scale is on the order of $10^{-3}$ s while the spin-spin interaction is on the order of $10^{-7}$ s.

### 4.2 Stoner Theory

The Stoner theory [Stoner (1938)] marked a major advancement in the understanding of itinerant electron magnetism. It offered, for the first time, a reasonable explanation for the fractional moment exhibited by certain ferromagnets, in particular nickel. Still, at the time there were recognized shortcomings. Most glaring was the over-estimation of $T_C$ and the lack of a Curie-Weiss type susceptibility seen in practically all ferromagnetic materials. The source of these problems lies in the total reliance on the Fermi function for the temperature dependence of the thermodynamic quantities. Still, despite its obvious flaws, the Stoner theory has become the basis for all major theoretical advancements in itinerant magnetism. This theory is a mean field approach to magnetic order. The main difference between the itinerant Stoner theory and the local moment Weiss theory begins with the Weiss assumption that the electrons are localized and occupy $m_J$ dependent energy levels. The Stoner theory considers the electrons to be delocalized, moving about in the periodic potential of the crystal lattice. The crystal fields quench the orbital moment of the conduction electrons and the good quantum numbers include the $k$ and the spin.

Stoner theory is based on three postulates: 1) the magnetic carriers are unsaturated spins in the $d$-band, 2) effects of the exchange are treated in a mean field way, and 3) Fermi statistics must be followed. A simple explanation of the Stoner theory can be offered by considering a parabolic conduction band. The band can be split into two subbands each containing only one type of spin. If a mean field which incorporates all interactions is introduced, the strength per atom is given by

$$H_M = NM = NM_0 \phi$$  \hspace{1cm} (4.1)
where $\varphi = M/M_0$. The energy shift due to the mean field is

$$\epsilon_m = -\mu_B H M = -\mu_B N M_0 \varphi = -k_B \Theta \varphi. \quad (4.2)$$

This defines a temperature, $\Theta$, which is characteristic of the material and equal to $\mu_B N M_0 / k_B$.

Realizing that the field can be expressed as $dF/dM$ allows the free energy contribution per electron of the mean field at $T = 0$ K ($E_m/n$) to be determined.

$$\frac{E_m}{n} = -\int H dM = -\frac{1}{2} k_B \Theta \varphi^2 \quad (4.3)$$

This is the energy reduction induced by polarizing the conduction band electrons. The different spin subbands are now split relative to one another. Due to the need to have an equal chemical potential for both spin directions (as they are in the same metal) causes the subband with a moment parallel to the applied field to have a larger population. Defining $n^+$ and $n^-$ as the parallel and antiparallel moment populations respectively the following relations exist.

$$n^+ + n^- = n \quad (4.4)$$

$$n \varphi = n^+ - n^- \quad (4.5)$$

$$n^\pm = \frac{n}{2} (1 \pm \varphi) \quad (4.6)$$

The populations are given by

$$\frac{n}{2} = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (4.7)$$

$$\frac{n}{2} (1 \pm \varphi) = \int_0^{\epsilon_F^\pm} g(\epsilon)d\epsilon \quad (4.8)$$

The previous equation can be rewritten as two integrals

$$\frac{n}{2} \varphi = \int_{\epsilon_F}^{\epsilon_F^+} g(\epsilon)d\epsilon \quad (4.9)$$
and

\[ \frac{n}{2} \phi = \int_{-\infty}^{\infty} g(\epsilon) d\epsilon \]  

with the use of Eq. 4.7. In the parabolic band the density of states, \( g(\epsilon) \), varies like \( \sqrt{\epsilon} \) and the energy of the spin splitting is given by

\[ \epsilon^\pm = \epsilon_F (1 \pm \phi)^{2/3}. \]  

The band energy change due to this splitting can be determined by integrating over occupied states to give

\[ E_b = \int_{\epsilon_F^-}^{\epsilon_F^+} \epsilon g(\epsilon) d\epsilon - \int_{\epsilon_F^-}^{\epsilon_F^+} \epsilon g(\epsilon) d\epsilon. \]  

If \( \epsilon^\pm \) is given by Eqs. 4.9-4.11 then

\[ E_b = \frac{3}{10} n \epsilon_F \left[ (1 + \phi)^{5/3} + (1 - \phi)^{5/3} \right]. \]  

This is the increase in energy caused by polarizing the conduction band electrons. Since the electrons are fermions, the polarization requires a promotion of antiparallel moments to the unoccupied, higher energies so that they may switch to a parallel orientation. The free energy is now given by

\[ E = E_b + E_m = E(\phi) = \frac{3}{10} n \epsilon_F \left[ (1 + \phi)^{5/3} - (1 - \phi)^{5/3} \right] - \frac{1}{2} k_B \Theta \phi^2 + E_0. \]  

\( E_0 \) contains all other terms in the free energy not explicitly related to the mean field effects. An extremum for Eq. 4.14 is found by setting \( dE(\phi)/d\phi \) equal to 0. Doing this gives

\[ \epsilon^+ - \epsilon^- = 2k_B \Theta \phi = \Delta E \]  

\( \Delta E \) is the band splitting, also referred to as the Stoner gap energy. It is the energy introduced by the mean field. The two extreme situations are \( \phi \to 0 \) and \( \phi \to 1 \). Combining Eqs. 4.11
and 4.15 the two limits on the magnetization can be explored.

\[ \varphi = 0 \Rightarrow \frac{k_B \Theta}{\epsilon_F} = \frac{2}{3} \]  
\[ \varphi = 1 \Rightarrow \frac{k_B \Theta}{\epsilon_F} = \frac{1}{\sqrt{2}} \]  

These two results define three ranges of magnetic order. For the lower threshold where \( \frac{k_B \Theta}{\epsilon_F} < \frac{2}{3} \) no magnetic order exists. This is the case for palladium. The intermediate range where \( \frac{2}{3} < \frac{k_B \Theta}{\epsilon_F} < \frac{1}{\sqrt{2}} \) there is magnetic order but the exchange is insufficient to saturate the spins and the system is weakly ferromagnetic. This corresponds to ZrZn\(_2\). In the upper bound, for \( \frac{k_B \Theta}{\epsilon_F} \geq \frac{1}{\sqrt{2}} \), the system is strongly ferromagnetic as is the case for Ni.

Based on the free energy it is possible to calculate the inverse susceptibility as the second derivative of Eq. 4.14 with respect to \( \varphi \). Doing so gives

\[ \frac{n^2 \mu_B^2}{\chi} = \frac{n^2}{4} \left( \frac{1}{g(\epsilon^+)} + \frac{1}{g(\epsilon^-)} \right) - nk_B \Theta. \]  

If the free energy is to be a minimum, Eq. 4.18 must be positive which helps provide a criterion for spontaneous magnetic order. When \( \varphi = 0 \) the free energy must have a maximum so that as \( \varphi \) increases \( E(\varphi) \) decreases and the moment bearing state is favored. In the non-magnetic case it is obvious that \( g(\epsilon^+) = g(\epsilon^-) = g(\epsilon_F) \). As the spontaneous moment increases the inverse susceptibility must decrease. This gives rise to the so-called Stoner criterion for spontaneous magnetism

\[ \frac{2}{n} g(\epsilon_F) k_B \Theta \geq 1. \]  

In order to satisfy the Stoner criterion a system needs to have either a large density of states at the Fermi energy or a large interaction term, \( k_B \Theta \). It turns out that the interaction term is an atomic property and is largely unaffected by chemistry, so the density of states in the metal is the dominant mechanism by which Eq. 4.19 is met. In practice a parabolic, free-electron like band will never have a density of states large enough for this to happen, so that assumption will have to be abandoned.
To determine the temperature dependence of the magnetization and the susceptibility the populations of the two subbands is written as

\[ n^{\pm} = \int_{0}^{\infty} \frac{g(\epsilon)}{\exp\left(\frac{\epsilon - \eta^{\pm}}{k_B T}\right) + 1} \, d\epsilon \]  

(4.20)

where \( \eta^{\pm} \) is the sum of the chemical potential, interaction energy, and Zeeman energy from an externally applied field.

\[ \eta^{\pm} = \mu \pm k_B \Theta \varphi \pm \mu_B H_{ext} \]  

(4.21)

Combining Eqs. 4.6 and 4.20 allows for the calculation of the magnetization \( M \) given by

\[ M = n\mu_B \varphi. \]  

(4.22)

Doing this gives a magnetic moment of

\[ M = 2\mu_B \left( \mu_B H_{ext} + k_B \Theta \frac{M}{n\mu_B} \right) \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon \]  

(4.23)

with \( f(\epsilon) \) being the Fermi function. This can be rather simply solved for \( M \) explicitly to give

\[ M = \frac{2\mu_B^2 H_{ext} \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon}{1 - \frac{2k_B \Theta}{\mu} \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon} \]  

(4.24)

The (dc, zero field limit) susceptibility can be found by taking \( \chi = M/H_{ext} \). This gives

\[ \chi = \frac{2\mu_B^2 \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon}{1 - \frac{2k_B \Theta}{\mu} \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon}. \]  

(4.25)

The condition for spontaneous ferromagnetism is that the inverse susceptibility go to zero at a finite temperature. This condition is met when

\[ \frac{2k_B \Theta}{\mu} \int_{0}^{\infty} g(\epsilon) \left| \frac{df(\epsilon)}{d\epsilon} \right| d\epsilon = 1. \]  

(4.26)
The temperature dependence implied by the above equation is given by

$$2g(\epsilon_F)k_B\Theta \left(1 + aT_C^2\right) = 1. \quad (4.27)$$

The coefficient $a$ is related to the characteristic Fermi degeneracy temperature and is given by

$$a = \frac{\pi^2}{6}k_B^2 \left(\frac{g'(\epsilon_F)}{g(\epsilon_F)} - \left(\frac{g(\epsilon_F)'}{g(\epsilon_F)}\right)^2\right) \quad (4.28)$$

which comes from the Sommerfield expansion. If $T_C << T_F$ then Eq. 4.27 can be expressed as

$$k_B\Theta = \frac{n}{2g(\epsilon_F)} \left(1 + \frac{T_C^2}{T_F^2}\right). \quad (4.29)$$

To determine the behavior of the magnetization as temperature is varied the susceptibility from Eq. 4.18 is revisited and another Sommerfield expansion is done to pull out a magnetization dependence in $\chi$.

$$\frac{n^2 \mu_B^2}{\chi} = \frac{n^2}{2g(\epsilon_F)} \left(1 - c\varphi^2\right) - nk_B\Theta \quad (4.30)$$

The coefficient $c$ is given by

$$c = \frac{1}{8} \frac{n^2}{g(\epsilon_F)^2} \left[\frac{g''(\epsilon_F)}{g(\epsilon_F)} - 3 \left(\frac{g'(\epsilon_F)}{g(\epsilon_F)}\right)^2\right]. \quad (4.31)$$

For equilibrium

$$k_B\Theta = \frac{n}{2g(\epsilon_F)} \left(1 - \frac{1}{3}c\varphi^2\right). \quad (4.32)$$

If there is a minimum in $\chi$ for zero moment, then as the moment grows

$$\frac{2}{n}g(\epsilon_F)k_B\Theta \leq 1 - \frac{1}{3}c\varphi^2. \quad (4.33)$$

A negative value of $c$ fulfills this condition for all values of $\varphi$. This occurs when the Fermi
energy is at a maximum in the density of states. Under this umbrella

\[ k_B \Theta = \frac{n}{2g(\epsilon_F)} \left( 1 + \frac{1}{3}|c|\varphi^2 \right) \]  

Equating similar terms in Eqs. 4.29 and 4.34 allows for a determination of how the Curie temperature scales with magnetization. Equating like terms from both expressions gives

\[ \varphi^2 = \frac{3}{|c|} \frac{T_C^2}{T_F^2} \]  

This shows that in the Stoner model the Curie temperature scales linearly with the magnetization, and it is expected that systems with larger magnetizations will have higher Curie temperatures.

In the case of very weak itinerant ferromagnets (\( \varphi << 1 \)) it is possible to expand Eq. 4.20 in powers of \( \varphi \). To first order at zero temperature this gives

\[ \frac{2}{n} g(\epsilon_F) (k_B \Theta \varphi + \mu_B H_{ext}) = \varphi \]  

Using the temperature dependencies of the coefficients \( a \) and \( c \) to substitute for the \( T = 0 \) value of \( \varphi \) leads to

\[ \frac{2}{n} g(\epsilon_F) (k_B \Theta \varphi + \mu_B H_{ext}) = \varphi (1 - aT^2) - \frac{1}{3} c\varphi^3. \]  

When \( c \) and \( a \) are both positive and using Eq. 4.35 where \( a = T_F^2 \) yields

\[ \frac{2}{n} g(\epsilon_F) k_B \Theta \varphi = 1 + \frac{1}{3} |c|\varphi^3, \]  

\[ |a|T_C^2 = \frac{1}{3} |c| \varphi_0^3, \]  

and

\[ \chi_0 = \frac{3\mu_B^2 g(\epsilon_F)}{|c| \varphi_0^2}. \]
Substituting Eq. 4.22 for $\varphi_0$ the magnetic isotherms for weak itinerant systems take the form

$$
\left( \frac{M(H, T)}{M(0, 0)} \right)^3 - \frac{M(H, T)}{M(0, 0)} \left( 1 - \frac{T^2}{T_C^2} \right) = \frac{2\chi_0 H}{M(0, 0)}.
$$

(4.41)

In zero applied field the square of the magnetization is seen to decrease like $T^2$ as the temperature is increased.

$$
M^2 = M(0, 0)^2 \left( 1 - \frac{T^2}{T_C^2} \right)
$$

(4.42)

Rewriting Eq. 4.41 and taking $dH/dM$ as the inverse susceptibility it is seen that

$$
\frac{1}{\chi} = \frac{3M^2}{2\chi_0 M_0^2} - \frac{1}{2\chi_0} \left( 1 - \frac{T^2}{T_C^2} \right).
$$

(4.43)

For the paramagnetic case, the magnetization vanishes and

$$
\chi = 2\chi_0 \left( \frac{T^2}{T_C^2} - 1 \right)^{-1}.
$$

(4.44)

In the ferromagnetic case the temperature dependence of $M$ must be considered. Doing this shows that the susceptibility in the ordered state varies like

$$
\chi = \chi_0 \left( 1 - \frac{T^2}{T_C^2} \right)^{-1}.
$$

(4.45)

The factor of 2 reduction in the susceptibility in the ordered state when compared with the paramagnetic state is a reflection of the assumption that above $T_C$ the magnetic moment vanishes completely. An applied field can be considered to create spins from a vacuum in the paramagnetic state. Below $T_C$, however, the field must flip a spin from (-) to (+) to induce a change in the moment.

### 4.3 Spin Fluctuations

The origin of the shortcomings in the Stoner model is its neglect of collective excitations. The only mechanism by which the magnetic moment can be destroyed is through single particle
spin flips across the Stoner gap. As was seen in the previous section, in order to account for
the observed magnetization the resulting gap implies a very large Curie temperature. An
attempt to rectify this problem is to try to consider how very low energy excitations in the
magnetization might be accommodated, much like spin waves in local moments. The newly
inherited problem is that without a lattice of moments it is much more difficult to establish the
waves. To sidestep this recourse to fluctuations of the spin density is made. It was first applied
to itinerant ferromagnets by Moriya and Kawabata (1973). A particularly clear derivation of
spin fluctuations is provided in Mohn (2003) which is followed here.

One definition of equilibrium is that the physical quantities which characterize the equilib-
rium are always very close to their average value. An alternative definition of an equilibrium
state is one in which the entropy, $S$, is maximized. The probability of a given macrostate being
realized may be written as

$$p(z) = A e^{S(z)}$$

where $z$ represents a quantity that characterizes the equilibrium and $A$ is a constant. A
constraint on $z$ is that it must not be forced constant by a conservation law. Taking the
equilibrium condition on $z$ to be $z = \langle z \rangle = 0$, if entropy is to be a maximum then

$$\frac{\partial S(z)}{\partial z} = 0$$

and

$$\frac{\partial^2 S(z)}{\partial z^2} < 0.$$  

With small $z$ and the above two conditions on the first and second derivatives a Taylor expansion of $S$ may be carried out and, up to second order

$$S(z) = S(0) - \frac{\nu}{2} z^2.$$  

This implies, with Eq. 4.46, that

\[ p(z)dz = Ae^{-\nu z^2/2}dz. \]  

\[ (4.50) \]

\( A \) may be calculated by requiring that \( \int p(z)dz = 1 \), that is the probability that the system is in some state is 1. Realizing that the probability is only significant for small values of \( z \) allows the integral to be evaluated over the range \(-\infty \) to \(+\infty \). Carrying out this integral gives

\[ A = \left( \frac{\nu}{2\pi} \right)^{\frac{1}{2}}. \]  

\[ (4.51) \]

Therefore, Eq. 4.50 is now given by

\[ p(z)dz = \left( \frac{\nu}{2\pi} \right)^{\frac{1}{2}} e^{-\nu z^2/2}dz. \]  

\[ (4.52) \]

This is a Gaussian distribution with a maximum at \( z = 0 \). With \( k \) equal to an integer

\[ \langle z^{2k} \rangle = \left( \frac{\nu}{2\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} z^{2k}e^{\nu z^2/2}dz = \nu^{-k}(2k-1)!!. \]  

\[ (4.53) \]

This means that \( \langle z^2 \rangle = \nu^{-1} \) and \( \langle z^4 \rangle = 3\nu^{-2} = 3\langle z^2 \rangle^2 \), and all even higher order average can be expressed in terms of \( \langle z^2 \rangle \). Armed with this knowledge, the fluctuations of the magnetic moment may now be explored.

Within a Landau theory of magnetic phase transitions the free energy can be written as

\[ F = aM^2 + \frac{b}{2}M^4 \]  

\[ (4.54) \]

where \( a = -\frac{1}{\chi_0} \left( 1 - \frac{T^2}{T_C^2} \right) \) and \( b = \frac{1}{\chi_0M_0} \) recalling the Stoner result. It should also be noted that within the Stoner framework \( T_C \) is of the order of \( 10^3 \) K. This leads to a neglect of the temperature dependence of the \( a \) term. As in the local moment case, by symmetry only even powers of the magnetization may appear, and \( M \) is often treated as a scalar quantity. However, the inclusion of fluctuations requires that attention be given to the vector nature of both \( M \) and
its fluctuations. Still, due to symmetry considerations the volume integral over odd powers in
the fluctuations vanishes always. Setting \( m(r) \) as the locally fluctuating moment it is assumed
\[
\frac{1}{V} \int (m(r))^n \, dV = (m^n) \text{ for } n = 2k
\]
while it is zero for \( n = 2k + 1 \).

For \( M \) pointing along some axis there will be two fluctuation directions perpendicular to
and one along \( M \). If \( M \) is taken parallel to the \( z \)-axis the three fluctuations may be written
as \( m_1 = m_x, \, m_2 = m_y, \) and \( m_3 = m_z \). The original order parameter in the free energy
(Eq. 4.54) can be replaced by the statistical average of the new order parameter, including the
fluctuations.
\[
M^{2n} \rightarrow \left\langle \left( M + \sum_{i=1}^{3} m_i \right)^{2n} \right\rangle
\]
Making this substitution, expanding, and setting the odd powers to zero gives
\[
F = a \left( M^2 + 2 \left\langle m_\perp^2 \right\rangle + \left\langle m_\parallel^2 \right\rangle \right) + \frac{b}{2} \left( M^4 + M^2 \left( 6 \left\langle m_\parallel^2 \right\rangle + 4 \left\langle m_\perp^2 \right\rangle \right) \right) + 8 \left\langle m_\perp^2 \right\rangle + 3 \left\langle m_\parallel^2 \right\rangle + 4 \left\langle m_\perp^2 \right\rangle \left\langle m_\parallel^2 \right\rangle
\]
In the above \( m_\perp \) and \( m_\parallel \) denote the fluctuations perpendicular and parallel to \( M \), respectively.
In the limit of zero temperature the fluctuation amplitude is zero and this reduces to Eq. 4.54.
Also, the dynamics of the fluctuations scale with the static susceptibility through the coefficients \( a \) and \( b \). Keeping with the Landau theory of phase transitions, the Curie temperature
corresponds to the temperature at which the susceptibility diverges (or the inverse suscepti-
bility is zero). There is the additional constraint that \( M = 0 \) which implies there is no longer
a difference between \( \left\langle m_\perp^2 \right\rangle \) and \( \left\langle m_\parallel^2 \right\rangle \). The inverse susceptibility is calculated by \( \chi^{-1} = \frac{\partial^2 F}{\partial M^2} \)
with \( M = 0 \) giving
\[
\chi^{-1} = 2a + 2b \times 10 \left\langle m^2 \right\rangle = 0.
\]
fluctuations is given by

$$\langle m_C^2 \rangle = \frac{M_0^2}{5} \quad (4.59)$$

Therefore, the amplitude of the fluctuations at the Curie temperature ($\langle m_C^2 \rangle$) is determined by ground state properties. Coupling Eq. 4.59 with the idea that the fluctuations must disappear for $T = 0$ the temperature dependence of the fluctuations can be determined. From the fluctuation-dissipation theorem classical fluctuations basically change linearly with temperature. Thus,

$$\langle m_{||}^2 \rangle (T) = \langle m_{\perp}^2 \rangle (T) \simeq \langle m_C^2 \rangle \frac{T}{T_C} = \frac{M_0^2}{5} \frac{T}{T_C} \quad (4.60)$$

is the approximate temperature variation in an isotropic system. From Eq. 4.57 $M(T)$ can be calculated directly by minimizing the free energy with respect to the magnetization. Setting $\partial F/\partial M = 0$ and substituting the expressions for $a$ and $b$ given just after Eq. 4.54 gives

$$M^2 = M_0^2 - 3 \langle m_{||}^2 \rangle + 2 \langle m_{\perp}^2 \rangle \quad (4.61)$$

If an isotropic system is assumed (Eq. 4.60) the resulting magnetization variation with temperature is

$$M^2(T) = M_0^2 \left(1 - \frac{T}{T_C}\right) \quad (4.62)$$

The more rapid decrease in $M$ as $T$ increases when compared with the Stoner result derives from the consideration of low energy excitations.

Examining the temperature behavior of the order parameter defined in Eq. 4.56 shows another positive feature associated with these spin density fluctuations.

$$\left\langle \left( \mathbf{M} + \sum_{i=1}^{3} \mathbf{m}_i \right)^2 \right\rangle = M_0^2 \left(1 - \frac{T}{T_C}\right) + 2 \langle m_{\perp}^2 \rangle + \langle m_{||}^2 \rangle \quad (4.63)$$

For temperatures less than $T_C$ (in an isotropic system) this gives

$$M_0^2 \left(1 - \frac{2}{5} \frac{T}{T_C}\right) \quad (4.64)$$
as the order parameter variation with temperature. For temperatures greater than \( T_C \) the right hand side of Eq. 4.63 is
\[
M_0^2 \frac{3}{5} \frac{T}{T_C}.
\]
(4.65)

This last result shows that even in the paramagnetic state, the order parameter is locally non-zero even though globally it averages to zero. This recalls a Curie-Wiess-like behavior for \( T > T_C \), which is commonly observed for many itinerant ferromagnets. This stands opposed to the Stoner result where the paramagnetic state is completely non-magnetic (other than as a usual metal).

From Eq. 4.58 it is possible to now determine an approximate temperature dependence for the susceptibility both above and below the ordering temperature.

\[
\chi(T) = \chi_0 \left(1 - \frac{T}{T_C}\right)^{-1} \text{ for } T < T_C,
\]
(4.66)

\[
\chi(T) = 2\chi_0 \left(\frac{T}{T_C} - 1\right)^{-1} \text{ for } T \geq T_C.
\]
(4.67)

A Curie constant can be extracted from this result as well which is
\[
C = \frac{d(\chi^{-1})}{dT} = \frac{1}{2\chi_0 T_C}.
\]
(4.68)

This is seen not to vary with temperature as it did in the Stoner model. Therefore, it reproduces the linear behavior observed in \( \chi^{-1} \) vs. \( T \) in the paramagnetic state.

The preceding work was developed for weakly ferromagnetic systems. Lonzarich and Taillefer (1985) extended this work to stronger ferromagnets and showed that in between the Stoner and spin fluctuations limits there is an intermediate strength where the temperature variation of the inverse susceptibility is like \( T^{4/3} \). In all cases, though, the magnetic susceptibility decreases as temperature decreases. This is in direct opposition to the experimentally observed results in the TDR data.
4.4 Semi-Phenomenological Model of Itinerant Ferromagnets

The development of the Stoner theory [Stoner (1938)] was driven by a desire to understand how a fractional Bohr magneton magnetic moment could be created in nickel. The failures of Stoner theory, \textit{i.e.} Curie temperatures that are too high and the lack of a Curie-Weiss susceptibility above $T_C$, were impetus for the development of the spin fluctuation theory of Moriya and Kawabata [Moriya and Kawabata (1973)]. While spin fluctuation theory does predict a Curie-Weiss type paramagnetic state and largely correct the Curie temperatures, neither it nor the Stoner theory adequately describe the broad maximum seen in the rf data. Indeed, both theories derive a strictly zero field limit of $\chi$ just below $T_C$ of the same form

$$\chi(T < T_C) = \chi_0 \left( 1 - \left( \frac{T}{T_C} \right)^n \right)^{-1}. \quad (4.69)$$

The difference between the two theories is the value of $n$. For Stoner theory $n = 2$ while for spin fluctuations $n = 1$ [Mohn (2003)]. There is an intermediate regime where $n = 4/3$ [Lonzarich and Taillefer (1985)]. The Stoner theory does predict a nonzero $\chi$ at $T = 0$ and $H = 0$ [Wohlfarth (1968)].

A zero field limit calculation, however, is not representative of a ferromagnetic system below $T_C$. As the system begins to order there is a non-zero field in the sample from the ordered moments themselves. It is interesting that this internal field, which has been incorporated into the theory to account for the ordering is neglected in calculations of the magnetic susceptibility. In itinerant systems this mean field should continue to increase as $T$ decreases and the fraction of spin polarized conduction electrons increases. The increase in the itinerant mean field may be expected to be more dramatic than in a local moment mean field because in the former there are physically more magnetic carriers as temperature decreases, while in the latter there is merely less thermal randomization of the moment directions. To account for the self-field a modified Brillouin function for a spin-1/2 system in a magnetic field is proposed [Vannette and Prozorov (2008)]. A spin-1/2 system is chosen because in itinerant systems it is the single electron spin that is of interest.
\[ m^*(t, h) = m_0^* \frac{\ln (1 - n)}{1 - n}. \] (4.70)

In the above equation, \( t = \frac{T}{T^*} \) where \( T^* \) is a characteristic temperature not necessarily equal to \( T_C \) and \( h \) is a dimensionless field term. It should be noted that this form does not represent the magnetization of the sample. Rather, \( m^* \) may be taken as some measure of the unpolarized fraction of the conduction band. Differentiating with respect to \( h \) gives

\[ \chi(t, h) = \frac{\chi_0}{1 - n} \frac{\ln (1 - n)}{1 - n}. \] (4.71)

In the limit \( h \to 0 \), this reduces to Eq. 4.69 if \( T^* \to T_C \), even though we are not beginning with the proper form for the magnetization.

Figure 4.3 presents the calculated curves for \( m^* \) from Eq. 4.70, \( 1 - m^* \), and \( \chi \) from Eq. 4.71. The observed behavior of \( 1 - m^* \) is qualitatively similar to the expected magnetization versus temperature curve. The susceptibility curve shows the basic features seen in the TDR data in the itinerant systems, as presented below.

As a test of the validity of the assumptions in the proposed model, measurements on
YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$ were made. These compounds are part of the $RT_2Zn_{20}$ family, some of which show extreme Stoner enhancement of the conduction band. Jia et al. (2007) showed that YFe$_2$Zn$_{20}$ has a Stoner $Z$ approaching the ferromagnetic limit while YCo$_2$Zn$_{20}$ has a $Z$ closer to copper. The small $Z$ found in the cobalt compound suggests that TDR measurements of $\chi$ from YCo$_2$Zn$_{20}$ should show a resistive signal. The large $Z$ in YFe$_2$Zn$_{20}$ suggests that TDR measurements of $\chi$ should be resistive, with an enhancement due to the large fluctuations associated with proximity to ferromagnetic order. In order to facilitate a more accurate comparison between the two materials, samples of similar size and shape leading to similar filling factors. Figure 4.4 shows the measured change in susceptibility relative to 2 K for YCo$_2$Zn$_{20}$ and YFe$_2$Zn$_{20}$. Both samples show a monotonic increase in $\chi$ consistent with the resistive behavior [Jia (2008)]. The inset to Fig. 4.4 shows the measured absolute change in $\chi$ for the same two samples. The iron containing compound has a much higher measured $\chi$ when compared to the cobalt containing compound. The larger absolute susceptibility in YFe$_2$Zn$_{20}$ offers confirmation that the measured $\chi$ does reflect the effects of magnetic fluctuations in the conduction band.
Figure 4.4 Main panel: Change in measured susceptibility for YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$. Inset: Measured susceptibility for the same two compounds on an absolute scale.

4.5 Materials Studied

4.5.1 ZrZn$_2$

Ferromagnetism in ZrZn$_2$ was discovered Matthias and Bozorth in 1958 [Matthias and Bozorth (1958)]. It was a surprising development as this was the first transition metal compound to manifest magnetic order that did not contain Fe, Ni, Co, Cr, or Mn. The only mechanism that could be invoked for the observed small magnetic moment of 0.13 $\mu_B$ per formula unit was through conduction band polarization. Since the time of the discovery of ferromagnetic order the saturated moment has shifted up to 0.17 $\mu_B$ per formula unit and the Curie temperature has shifted down to about 28 K. The fields applied to measure the magnetic moment in the original paper are believed to be on the order of 5 kOe. The only notation is in the graph of the data where “H=3,900” and “H=10,800” are labels on the two magnetization curves. If the units are oersted then the large applied fields could easily shift the observed transition temperature up.
Given that both Zr and Zn are superconductors there was a good deal of effort put in searching for superconductivity in the 1-2 compound. In 2001 the coexistence of superconductivity and ferromagnetism in the compound was reported for temperatures less than 290 mK [Pfleiderer et al. (2001)]. Later it was determined that the process involved in preparing the sample for measurement (spark erosion cutting) resulted in a surface layer that is zinc deficient. This surface alloy with less zinc than ZrZn$_2$ was responsible for the observed superconductivity [Yelland et al. (2005a)].

In the mistaken observation of superconductivity, the low frequency ac susceptibility was measured and the presented data are said to have a “temperature independent background” due to the ferromagnetic ordering subtracted [Pfleiderer et al. (2001)]. No actual frequency value was reported; it was just stated that the frequency was “low.” In the later paper [Yelland et al. (2005a)] the low temperature ac susceptibility measured at 1.17 kHz is presented for the spark cut sample. At approximately 200 mK there is a sharp increase in $\chi'$ and $T_{sc}$, the superconducting transition temperature, is indicated at 600 mK. A large value of the susceptibility in the normal state is ascribed to the ferromagnetism. The field dependent susceptibility is also presented for two temperatures (1.6 K and 50 mK). On the scale presented (arbitrary units in $\chi'$ and 0.5-2 T for applied field) there is no observable change in the higher temperature (FM state) data. The data presented in these two papers exhausts the reported low frequency ac susceptibility in ZrZn$_2$.

Figure 4.5 presents the rf susceptibility for single crystal ZrZn$_2$ in applied dc fields. The behavior of $\chi$ at the radio frequencies stands in stark contrast to the accepted local moment systems (Ch. 2). Whereas the local moment systems manifest a strong, well-defined peak in $\chi$ at $T_C$ which shifts to higher temperatures in applied fields, the itinerant system exhibits a broad maximum in $\chi$ below $T_C$ which shifts to lower temperatures as field is applied. This difference was first reported in 2008 [Vannette et al. (2008d)]. The inset to Fig. 4.5 shows that at $T_C$ a local maximum is absent.

The low temperature resistivity of ZrZn$_2$ exhibits unusual $T^{5/3}$ behavior [Yelland et al. (2005b)]. Fig. 4.6 shows $(1 + 4\pi \chi)^2$ for ZrZn$_2$ in an applied field of 1.2 kOe vs. $T^{5/3}$. The solid
Figure 4.5 $\chi$ vs. $T$ for the weak itinerant ferromagnet ZrZn$_2$ in various applied dc fields. Fields are given in Oe.

The line is the data and the dashed line is a calculated $\rho_0 + AT^{5/3}$ curve. The low temperature data are seen to fall on the calculated curve, showing that the measure $\chi$ in this field is a direct probe of the behavior of the resistivity with essentially no contribution from the spins. In this case, the spin component of the susceptibility has been suppressed below the level of detection. The inset to Fig. 4.6 is the full scale resistivity vs. temperature in the same field. The fact that the resistivity in this field is consistent with the zero field behavior will be of use in analyzing the spin component of the measured $\chi$.

4.5.2 Y$_9$Co$_7$

Y$_9$Co$_7$ has been reported to show itinerant ferromagnetism at 4.5 K as determined by a maximum in heat capacity, low frequency ac susceptibility, and magnetization studies [Sarkissian and Grover (1982), Yamaguchi et al. (1984)]. Further, at approximately 3 K this material enters a superconducting state. There is one study [Rastogi and Coles (1985)] that suggests this compound is not truly ferromagnetic, however the consensus in the sparse literature is that
long range ferromagnetic order does exist here, and the purity of the starting elements is a powerful indicator of whether or not the FM order is manifest. TDR measurements (Fig. 4.7) suggest the itinerant ferromagnetism sets in at a much higher temperature, if the data are assumed to be consistent with ZrZn$_2$ and the yet to be discussed GdFe$_2$Zn$_{20}$ pure and doped series of compounds. Unlike the other samples studied in this work, the data presented on Y$_9$Co$_7$ is from a polycrystalline sample provided by researchers at Los Alamos National Labs.

4.5.3 Half-Band Ferromagnet NiMnSb

NiMnSb is an example of the so-called half-band ferromagnets. These are materials that are supposed to exhibit complete polarization of the conduction band at low temperatures [de Groot et al. (1983)]. They are sometimes referred to as half-metallic systems as one spin-subband is metallic while the other is gapped at zero temperature. Recently the question of whether or not these materials truly are half metallic has been raised [Dowben and Skomski (2004)], but this point is not relevant for the current work. The experimental fact that NiMnSb

Figure 4.6 Arbitrary $\rho$ vs. $T^{5/3}$ for ZrZn$_2$ in a 1.2 kOe applied field (solid line) and calculated $\rho_0 + AT^{5/3}$ (dashed line). Inset: $\rho$ vs $T$ up to 40 K.
is a full moment ferromagnet coupled with the suspicion that it is a band magnet is motivation to attempt a zero field measurement. This material has a Curie temperature of approximately 730 K. A plot of as measured susceptibility of NiMnSb along with a measurement of the background due to the empty sample holder is presented in Fig. 4.8. At the ordering temperature a dramatic drop in $\chi$ is evident. What is noticeably absent is evidence of a peak-like structure as seen in yttrium-iron-garnet presented in the local moment chapter (Fig. 2.29). In any case, like with Ni, it is difficult to envision a scenario whereby the resistance of a metal will dramatically decrease with increasing temperatures for $T > 700$ K. If $\chi$ at the highest temperature is dominated completely by the sample holder, then it is reasonable to set the values at this point in the two runs as equal and subtract the sample holder contribution. This approximation is supported by the observation that the induced frequency shift from room temperature to 700 K is approximately the same for both the empty sample holder and the sample plus holder runs. Assuming the contributions of the two pieces simply add, we can subtract the frequency shift due to the holder from the NiMnSb run to get an idea of what the sample response is. This is presented in Fig. 4.9.

Figure 4.7 $\chi$ vs. $T$ for Y$_9$Co$_7$ in four applied fields. SC, FM, and PM denote the superconducting, ferromagnetic, and paramagnetic states, respectively.
Figure 4.8 Plot of $\chi$ vs. $T$ for NiMnSb and the empty Inferno sample holder.

Figure 4.9 Magnetic susceptibility of NiMnSb with the sample holder contribution subtracted.
The behavior of NiMnSb stands in some contrast with the ZrZn\(_2\) data in that there is no obvious maximum in \(\chi\) well below \(T_C\). This may be an artifact of the background subtraction process in NiMnSb, or it may be real effect hinting at the possibility that this material shows at least some local moment character. The contrast between NiMnSb and yttrium-iron garnet (Fig. 2.29) at \(T_C\) is obvious, though. Whereas the insulator shows a well defined peak, the half-band magnet only shows a rapid increase in \(\chi\) followed by a gradual decrease. This is consistent with GdFe\(_2\)Zn\(_{20}\), presented in Ch. 5. Taken together, these data suggest that there is a certain degree of localization in NiMnSb.

### 4.6 Analysis of ZrZn\(_2\) and Y\(_9\)Co\(_7\)

An attempt to fit the model developed to explain the data in itinerant systems is made. However, there is the problem that the as measured susceptibility contains a resistivity component. This must be dealt with in a reasonable manner in order to explore the magnetic effect. From Fig. 4.6 it is evident that the application of a 1.2 kOe field is insufficient to invoke a significant change in the \(\rho(T)\) behavior in ZrZn\(_2\), going so far as to recover the \(T^{5/3}\) response. Therefore it is reasonable to assume that the resistivity will not be affected by lower fields.

To account for the resistivity contribution to the measured susceptibility in ZrZn\(_2\), data collected in a dc field of 1 kOe were subtracted from lower field runs. This field was sufficiently large to completely suppress the maximum in \(\chi\) while being small enough that it is not expected to result in a significant magnetoresistance.

Data fits to the model were attempted for various values of \(n\). It was found that \(n = 1\), corresponding to the spin fluctuations theory, gave the best agreement. Figure 4.10 shows best fits of Eq. 4.71 to the TDR data for ZrZn\(_2\). The best fit was determined by minimizing the sum of the squared differences between the data points and the fit curve at constant temperature. The resulting values of the fitting parameters are shown in Fig. 4.11. \(\chi_0\) decreases with applied \(H\). \(T^*\) is constant within the errors and it is approximately equal to \(T_C\). The value of \(h\) is approximately constant up to applied fields of about 125 Oe and thereafter grows monotonically as \(H\) is increased. Fields for which \(h\) increases are those where the fits become
worse. Even though the higher field data are not well recreated by the model, the fact that the lower non-zero field data are fit reasonably suggests that this is a good direction to explore for understanding of this observation.

Figure 4.10 Fits of ZrZn$_2$ data to Eq. 4.71.

Similar fitting was done on the Y$_9$Co$_7$ sample in the ferromagnetic state. Results of those fits are shown in Fig. 4.12. Again, $n = 1$ was found to give the best fit for the data. Figure 4.13 shows the fit parameters for the Y$_9$Co$_7$ data. At the low temperature end, the superconducting state is beginning to compete more aggressively with the ferromagnetism, and the zero field data shows a strong deviation. This deviation is less pronounced as the applied field increases. Interestingly, if $T^*$ is assigned the value of $T_C$ as is apparently the case from the ZrZn$_2$ data, then this suggests that the Curie temperature for this compound is nearly 9 K. This is more than two times larger than what was previously thought. Curiously, even though both systems show strikingly different transition temperatures, and very different suppression fields, the effective fields from the fitting are approximately the same.

Both systems that are fit to this model exhibit very large error bars (±10% or more). However, given that this behavior was not predicted by the successful theories on itinerant systems, the fact that the model comes this close is intriguing. It is highly likely that the true
Figure 4.11 ZrZn$_2$ fit parameters with estimated errors.

Figure 4.12 Comparison of data (points) and fit (lines) for three applied fields in a polycrystalline sample of Y$_9$Co$_7$. 

behavior is nothing like a hyperbolic cosine. This is only meant to serve as a starting point giving the general direction in which to look for solutions to this theoretical problem.

4.7 Field Dependent $\chi$ in ZrZn$_2$ and Y$_9$Co$_7$

In contrast to the local moment behavior for GdPtIn and CeAgSb$_3$ the itinerant ferromagnets ZrZn$_2$ and Y$_9$Co$_7$ show dramatically decreasing susceptibility with applied field at a fixed temperature. This behavior is consistent with the interpretation that the measured susceptibility is, in fact, probing the spin fluctuating component of the magnetism invoked for CeVSb$_3$. The difference between the ZrZn$_2$ $\chi(H)$ (Fig. 4.14) data and that of GdPtIn or CeAgSb$_2$ is immediately evident. It is also grossly similar to the CeVSb$_3$ data in that the application of field reduces the measured susceptibility. Since ZrZn$_2$ is a known itinerant magnet with a highly polarizable conduction band, a solid interpretation of the data is that the TDR does measure the spin fluctuations in this compound.

Figure 4.15 shows the $\chi(H)$ data for Y$_9$Co$_7$ sample at different temperatures. The lowest temperature sweep at 1.9 K is into the superconducting phase and the applied field increases the susceptibility as the diamagnetic screening is weakened. The data at 6.1 K shows a well defined

![Figure 4.13](image-url)
Figure 4.14 \( \chi \) vs. \( H \) for ZrZn\(_2\) at 3.7 K.

Figure 4.15 \( \chi \) vs. \( H \) for Y\(_3\)Co\(_7\) at different temperatures.
peak at zero field which is rapidly suppressed with increasing field. At higher temperatures (9.5 and 15.3 K) the measured susceptibility is essentially flat with field. The rapidly decreasing peak in $\chi$ with field at the intermediate temperature supports the idea that the sample is in the ferromagnetic state up to this temperature. Offering assurance is the observation that at higher temperatures, this peak is absent.

Coupling these observations together, a case may be made that a Stoner enhanced conduction band manifests itself as an initial decrease in $\chi$ with applied field. The characteristic energy associated with the enhancement must be on the order of the thermal energy for the behavior to be observed. This is supported by both ZrZn$_2$ and Y$_9$Co$_7$ field sweeps at low temperatures. In the ordered state, where the Stoner enhancement is large enough to push the sample ferromagnetic, the susceptibility rapidly decreases with increasing field. Later, it will be seen that for doped GdFe$_2$Zn$_{20}$ the susceptibility also decreases with increasing field up to the ordering temperature. Above this temperature the susceptibility shows an increase with increasing field which is loosely in keeping with the domain argument presented for the local moment systems.

### 4.8 Summary

The sensitivity of TDR measurements to changes in $\chi$ has been applied to itinerant ferromagnetic systems. In contrast to local moment systems, the ordered state response of the magnetic susceptibility shows a broad maximum which suppresses in applied field and shifts to lower temperatures. Comparison with dc measurements show that the observed response is not the result of residing in the static regime. Conventional theories do not adequately predict nor describe the observed effect. A model based on the presence of a fluctuating component of the conduction band was proposed and fits the data for ZrZn$_2$ and Y$_9$Co$_7$ reasonably well. The validity of the model is further confirmed by comparison of measurements of the non–magnetic, Stoner enhanced YFe$_2$Zn$_{20}$ and non–magnetic, non–enhanced YCo$_2$Zn$_{20}$ compounds.
CHAPTER 5. Magnetic Susceptibility of Selected Members of $RT_2Zn_{20}$

5.1 Introduction

In metallic ferromagnets there is always the question of whether a particular system is itinerant or local in character. The absence of a theory that simultaneously explains both the local moment and itinerant magnetism is a long standing problem in condensed matter physics. A major step in the phenomenology of local moment vs. itinerant magnetism was the Rhodes–Wholfarth (RW) theory [Rhodes and Wohlfarth (1963)]. Under this theory one plots the ratio of the paramagnetic moment per ion to the saturated moment per ion in the ordered state against transition temperature for any ferromagnet. Materials showing a large RW ratio are candidate itinerant systems, while those with RW ratios close to 1 are likely local moment systems. It is seen that most materials have moderate RW ratios, indicating that most materials manifest properties seen in both local moment and itinerant magnets. The experimentally observed relationship implied by the RW curve does not offer much insight into how the gap between itinerant and local moment physics might be crossed, however.

The first reasonably successful theory of itinerant magnetism may be attributed to Stoner [Stoner (1938)]. Improvements on the Stoner theory have been made, most notably the advent of the spin fluctuation theory [Moriya (1985)]. However, a discussion of whether or not a particular material manifests itinerant magnetism may be carried out under the terminology of the Stoner theory. By considering the effect of onsite electron–electron (e–e) repulsion, Stoner showed that under certain conditions it is energetically favorable for the conduction band in a metal to spontaneously spin polarize to a some degree. This polarization is responsible for the observed magnetic moment in itinerant ferromagnets. Even in the absence of a finite temperature conduction band polarization (i.e. a finite Curie temperature) the magnetic susceptibility,
\( \chi \), is enhanced due to the e–e interactions. The enhancement of \( \chi \) often is described by the so–called Stoner Z factor. The susceptibility enhancement is in comparison to the calculated susceptibility as determined by band structure calculations, for example, with e–e interactions switched off. The relationship between the enhanced \( \chi \) and the unenhanced \( \chi_0 \) is given by

\[
\chi = \frac{\chi_0}{1 - Z}
\]  

(5.1)

where \( \chi_0 \) is given by \( \mu_B g(E_F) \). \( Z = 1 \) is taken as the Stoner criterion for the onset of itinerant ferromagnetic order.

It would be beneficial to have a system whereby the itinerant component of the magnetism could be tuned from the Stoner limit to nearly pure local moment physics. Recently a series of dilute rare earth–transition metal compounds \( RT_2Zn_{20} \) was shown to have just such this tunable property [Jia et al. (2007)].

The properties of \( YFe_2Zn_{20}, YCo_2Zn_{20}, \) and \( Gd(Fe_{x}Co_{1-x})_2Zn_{20} \) have been studied in detail [Jia et al. (2007), Jia et al. (2008)]. \( YFe_2Zn_{20} \) is a highly Stoner enhanced paramagnet \( (Z \approx 0.89) \) while the isostructural \( YCo_2Zn_{20} \) is only weakly paramagnetic. High field (50 kOe) \( M/H \) vs. \( T \) data coupled with low temperature specific heat measurements suggest that by titrating Co into \( YFe_2Zn_{20} \) it is possible to continuously tune the Stoner \( Z \) from a value greater than that for Pd \( (Z \approx 0.83) \) to a value comparable to Cu \( (Z \approx 0.29) \). Substituting Gd for Y in either compound leads to long range magnetic order. In the case of \( GdFe_2Zn_{20} \) the Gd ions order ferromagnetically with a mixed local moment/itinerant Fe flavor at an astonishingly high 87 K, while for \( GdCo_2Zn_{20} \) the Gd ions settle into a local moment antiferromagnetic order at a more reasonable 5.7 K. The FM ordering temperature in \( GdFe_2Zn_{20} \) is surprising because the Gd–Gd separation is approximately 14 Å [Nasch et al. (1997)]. Such a large separation normally implies very weak coupling between the rare earth ions. However, it was found that the highly Stoner enhanced conduction band measured in \( YFe_2Zn_{20} \) leads to a enhances the RKKY interaction allowing for the high ordering temperature [Jia et al. (2007)]. Since the cobalt containing analogue lacks the greatly enhanced conduction band, the ordered state sets in at a more conventional temperature.
Similar to the yttirium compounds, it is possible to titrate cobalt into the GdFe$_2$Zn$_{20}$ host to study how the transition to GdCo$_2$Zn$_{20}$ progresses. Previous static measurements have shown that (a) the transition from FM to AFM order occurs only for fairly large Co concentrations ($\geq$75%), (b) the transition temperature decreases monotonically with increasing Co, and (c) Cobalt doping directly affects the magnetic sublattice by replacing iron atoms and simultaneously contributes one extra valence electron per formula unit. Since the details of the Stoner enhancement depend both on the conduction electron density of states and on the ion type, finding a method to affect the conduction band without directly influencing the magnetic sublattice would be beneficial. Aluminum doping on the zinc sites allows for just such a modification. Each aluminum ion replacing a zinc ion contributes one extra valence electron per formula unit, just as in Co doping. However, since the Zn appears to be a spectator in the magnetic order, Al doping is not expected to directly affect the magnetic Fe sublattice. A comparison of the two types of doping (Co→Fe and Al→Zn) may elucidate the different roles played by the conduction band and the magnetic sublattice in the order. Any measurement of a magnetic property will be a convolution of both the local moment rare earth and the itinerant transition metal, however. What is required is a method to deconvolve the two contributions. Measurements of the radio–frequency magnetic susceptibility have been demonstrated to provide a means of distinguishing between local moment and itinerant contributions in ferromagnetically ordered materials [Vannette et al. (2008d)].

5.2 Experimental Details

Single crystals were prepared by the flux growth technique [Canfield and Fisk (1992)] from a Zn–rich self flux and sample quality was determined from powder x–ray diffraction as described by Jia et al. (2008). Samples of the same approximate size and shape of Gd(Fe$_x$Co$_{1-x}$)$_2$Zn$_{20}$ with $x=0, 0.12, 0.25, 0.5, 0.75, and 1$, GdFe$_2$(Zn$_y$Al$_{1-y}$)$_{20}$ with $y=0, 0.005, 0.017, 0.021, and 0.049 were chosen. In addition samples of the non–magnetic YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$ were also tested for comparison. Figure 5.1 is a photograph of the 4.9% Al-doped sample.

Magnetic susceptibility ($\chi = dM/dH$) was measured via a sensitive tunnel diode resonator
Figure 5.1  Photograph of 4.9% doped GdFe$_2$(Zn$_y$Al$_{1-y}$)$_{20}$. 
(TDR) technique [VanDegrift (1975a); Vannette et al. (2008d)]. The sample is placed on a sapphire rod and into a coil which is part of an LC tank circuit. The tank circuit is driven by a tunnel diode biased to the region negative differential resistance. The diode acts as an AC power sustaining oscillations of the tank circuit at its natural resonant frequency. Proper design and construction results in a circuit that resonates in the tens of megahertz band with a stability better than 0.01 Hz over hours to days. It is straightforward to show that changes in the sample susceptibility are reflected in changes of the tank circuit resonant frequency by

\[ 4\pi \chi = -G \frac{\Delta f}{f_0}. \]  

(5.2)

In the above \( f_0 \) is the empty coil resonance, \( \Delta f = f_{in} - f_0 \) where \( f_{in} \) is the resonance with the sample inserted in the coil and \( G \) is a geometric constant related to sample shape, through the demagnetization factor \( N \), and the ratio of sample volume \( (V_s) \) to coil volume \( (V_c) \).

\[ G = \frac{V_s}{(1-N)V_c} \]  

(5.3)

Typical resolution to changes in \( \chi \) for a 1 mm\(^3\) sample is on the order of 1 part in \( 10^8 \). The amplitude of the rf field produced by the tank coil is on the order of 5–10 mOe. A probe field as small as this very weakly perturbs the system under study, allowing access to dynamic responses that may be completely suppressed by larger fields. The TDR used in this work is mounted on a \(^4\)He cryostat with a nominal temperature range of 2–300 K. Magnetic field was supplied by a small superconducting magnet in vacuum capable of applying fields up to 3 kOe. The base resonant frequency was 28 MHz. To minimize drift in the diode properties its temperature was stabilized at 8.000±0.005 K.

Due to the operating frequency, in metallic samples the measured susceptibility is composed of two parts. The first part corresponds to the slope a static \( M(H) \) curve at a given applied field. This component may be either paramagnetic or diamagnetic. If the sample is metallic there is a second, diamagnetic contribution from the normal state skin effect. In the absence of a significant spin component (relative permeability, \( \mu_r=1 \)) the skin effect contribution is
related to the DC resistivity of the sample by

\[ \delta = \sqrt{\frac{2\rho}{\mu f}} \]  

(5.4)

In magnetically active metals, as is the case here, the resulting signal is a convolution of the two contributions. It was shown by Prozorov et al. (2000) that for non–magnetic (\( \mu = 1 \)) superconducting rectangular plates the measured susceptibility can be related to the London penetration depth, \( \lambda \), via

\[ 4\pi \chi = 1 - \frac{\lambda}{R} \tanh \frac{R}{\lambda}. \]  

(5.5)

\( R \) is a constant related to the dimensions of the plate. Replacing the London penetration depth with the normal state skin depth, \( \delta \), and allowing for the possibility of a non–zero magnetic susceptibility (\( \mu \neq 1 \)) changes the above equation to

\[ 4\pi \chi = 1 - \frac{\mu \delta}{2R} \tanh \frac{2R}{\delta}. \]  

(5.6)

In general a determination of \( G \) in Eq. 5.2 is difficult owing to uncertainties in \( N \) and \( V_s \). Hence, definitive claims regarding the absolute susceptibility of a single sample should be treated with caution. However, by choosing samples of similar size and shape (as was done here) it is possible to draw conclusions with respect to the qualitative differences in \( \chi \) between samples.

5.3 Results and Discussion

5.3.1 Pure materials

Fig. 5.2 presents \( \chi \) vs. \( T \) for pure GdFe\(_2\)Zn\(_{20}\) and GdCo\(_2\)Zn\(_{20}\) in zero applied DC field. At \( T_C \approx 87 \) K the gadolinium ions order ferromagnetically in GdFe\(_2\)Zn\(_{20}\) [Jia et al. (2008)] and \( \chi \) exhibits a large increase followed by a slow decrease. GdCo\(_2\)Zn\(_{20}\) does not manifest any increase in \( \chi \) at \( T_N \approx 5.7 \) K where the gadolinium ions order antiferromagnetically Jia et al. (2008). Rather it shows a rapid decrease in the measured susceptibility upon cooling.
into the antiferromagnetic state. A difference in $\chi$ at megahertz frequencies between ferro- and antiferromagnetic materials at their ordering temperatures has been noted previously [Vannette et al. (2008d)]. The difference in $\chi$ is explained by the extremely weak perturbation field used here. Magnetic susceptibility is a measure of how the magnetic moment of a sample changes in response to a change in magnetic field. In ferromagnetic materials the exchange interaction favors parallel alignment of neighboring spins. Perturbations of one moment via an external field are transferred to neighboring moments through the exchange interaction. It is energetically favorable for the bulk moment of the sample to change in response to the applied field, in this case the rf field from the coil. Conversely, in antiferromagnets exchange interactions lead to antiparallel alignment of spins (in some configuration) giving rise to no net moment in the sample. If a particular ionic moment is gently perturbed the exchange interaction will dominate and no change in the bulk moment of the sample will occur. In the vicinity of an ordering temperature exchange energy and thermal energy are on equal footing. It is very easy to change the orientation of a given spin through the application of a magnetic field. This leads to an enhanced rf susceptibility in a ferromagnetic sample as $T \rightarrow T_C$. In antiferromagnets, however, it is energetically favorable for the spins to order without a bulk moment. Therefore the rf susceptibility experiences no enhancement as $T \rightarrow T_N$. The decrease in the measured $\chi$ is associated with a decrease in resistivity due to a loss of spin disorder scattering.

The large value of $\chi$ in the ordered state for GdFe$_2$Zn$_{20}$ has been attributed to the enhanced susceptibility of the conduction band Vannette et al. (2008d); Vannette and Prozorov (2008). Jia et al. (2007) have shown that non-magnetic YFe$_2$Zn$_{20}$ exhibits an extremely large Stoner Z (Eq. 5.1) placing it close to the Stoner limit for itinerant ferromagnetism. Substitution of Gd for Y results in ferromagnetic order setting in at 87 K. The exceptionally high ordering temperature for such a dilute local moment system was ascribed to the presence of a highly polarizable conduction band which enhances the RKKY interaction. Substitution of Co for Fe suppresses the polarizability so that the ordering occurs at 5 K, as might be expected for systems with such large magnetic ion separation. Further effect of the Co substitution is to
Figure 5.2 Comparison of $\Delta \chi$ vs. $T$ for GdCo$_2$Zn$_{20}$ (hollow symbols) and GdFe$_2$Zn$_{20}$ (solid symbols). Dotted lines mark $T_N$ and $T_C$ for the cobalt and iron compounds respectively.

change the coupling to antiferromagnetic. To verify that the behavior of the temperature dependent $\chi$ in GdFe$_2$Zn$_{20}$ is due to the highly polarizable conduction band, $\chi_{rf}(T)$ in zero field was measured in the the non-ordering analogues YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$. Results are presented in Fig. 5.3.

As the samples of YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$ were of similar size and shape it is possible to make a comparison of the absolute values of $\chi$ between the two. Both samples exhibit a diamagnetic signal from 2–50 K. The susceptibility of YFe$_2$Zn$_{20}$ is larger than that of YCo$_2$Zn$_{20}$ by more than a factor of 4 over the entire temperature range. A fraction of the differences in $\chi$ between the two compounds may be accounted for by the different resistivities of each. From 2-300 K YCo$_2$Zn$_{20}$ has a lower value of $\rho$ than YFe$_2$Zn$_{20}$. At 50 K the resistivity of YFe$_2$Zn$_{20}$ is approximately 10 $\mu\Omega$–cm while YCo$_2$Zn$_{20}$ has a resistivity of approximately 7 $\mu\Omega$–cm. The difference in $\rho$ between the two samples decreases with decreasing temperature. Based on these figures it is possible to estimate the difference in $\chi$ due to the difference in $\rho$ between the two samples.
Figure 5.3  Zero field $\chi_{rf}(T)$ for YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$.

Define $\chi_1$ ($\chi_2$) as the measured susceptibility of sample 1 (2) with resistivity $\rho_1$ ($\rho_2$), permeability $\mu_1$ ($\mu_2$), geometric constant $R_1$ ($R_2$) measured at frequency $f_1$ ($f_2$). Provided $\delta_{1,2}$, given by Eq. 5.4 is much smaller than $R_{1,2}$, then Eq. 5.6 reduces to

$$4\pi\chi_{1,2} = 1 - \frac{\mu_{1,2}\delta_{1,2}}{2R_{1,2}}.$$ (5.7)

Under the conditions that $\mu_1 = \mu_2$, $R_1 = R_2$, and $f_1 = f_2$ Eq. 5.7 may be written as

$$4\pi\chi_{1,2} = 1 - c\sqrt{\rho_{1,2}}.$$ (5.8)

It is straightforward to show that

$$\left|\frac{\chi_1 - \chi_2}{\chi_1}\right| = \left|\frac{\sqrt{\rho_1}}{\sqrt{\rho_2}} - \frac{\sqrt{\rho_2}}{\sqrt{\rho_1}}\right|.$$ (5.9)

Taking the iron compound as sample 1 and the cobalt compound as sample 2, at 50 K the right hand side of Eq. 5.9 is about 0.16. Using data collected with the TDR, the left hand
side of Eq. 5.9 is about 4.23. Only about 4\% of the observed difference in $\chi$ for YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$ can be accounted for through differences in $\rho$. Allowing for variations in $R$ and $f$ between samples and runs respectively only accounts for another 5–10\% of the observed difference. Hence, the majority of the observed difference in $\chi$ for the non-ordered yttrium compounds is attributed to the enhanced susceptibility of the conduction band in YFe$_2$Zn$_{20}$.

5.3.2 Cobalt doping

Figure 5.4 presents the change in $\chi$ vs. temperature for five different samples with differing cobalt concentrations. It is seen that as cobalt concentration increases, the magnetic ordering temperature decreases. The change in $\chi$ first increases then decreases with increasing cobalt concentration. Application of a DC magnetic field suppresses the change in susceptibility for all samples (Fig. 5.5). In some concentrations the application of magnetic field also uncovers other features. This is most evident in the 50\% cobalt doped sample where in fields of 0.6–1.1 kOe a well-defined peak in $\chi$ is observed in the vicinity of 20 K. Previous TDR rf susceptibility studies on other magnetic materials have shown that the presence of a well defined peak is indicative of the onset of local moment ferromagnetic order Vannette et al. (2008d,a); Vannette and Prozorov (2008). As the introduction of cobalt ions into the parent GdFe$_2$Zn$_{20}$ lattice has been shown to suppress the itinerant component of the magnetism, the observation of features strongly associated with local moment magnetic order is not surprising. The sharpness of the peak in the 75\% cobalt doped sample is strongly suggestive of a transition from itinerant to local moment behavior.

The sharp features seen in the 12\% and 50\% cobalt doped samples show very little temperature dependence on applied field. There is a very slight increase in the temperature of the peak which is likely due to the change in the FM ordering temperature in applied field. Conversely, the sharp feature in $\chi$ observed in the 75\% doped sample shows a negative temperature dependence on applied field. Published DC moment measurements suggest that the ordering in $x = 0.75$ Gd(Fe$_x$Co$_{1-x}$)$_2$Zn$_{20}$ is not conventional FM order [Jia et al. (2008)]. It was proposed that for high cobalt concentrations frustration sets in. The behavior $\chi(T)$ in
Figure 5.4 Change in the measured susceptibility vs. temperature for five cobalt concentration ranging from $x = 0$-0.75 in Gd(Fe$_x$Co$_{1-x}$)$_2$Zn$_{20}$. 

![Graph showing the change in measured susceptibility vs. temperature for five cobalt concentrations ranging from $x = 0$-0.75 in Gd(Fe$_x$Co$_{1-x}$)$_2$Zn$_{20}$](image-url)
Figure 5.5  $\chi$ vs. $T$ in different fields for the four Co concentrations studied here. Numbers next to each trace indicate the applied field in kOe. Strong local moment peaks are observed in all samples except for the 50% doping.
different fields for $x = 0.75$ observed here is consistent with frustration being present in this system. The onset of magnetic order near 10 K is determined by the Fe concentration and its contribution to the Stoner enhancement of the conduction band. However, the predominant interaction between Gd ions is antiferromagnetic due to the large cobalt concentration. The decrease in the temperature of the peak with applied field may be attributed to a suppression of the antiferromagnetic coupling from the applied field.

5.3.3 Aluminum doping

For comparison, a series of aluminum doped GdFe$_2$Zn$_{20}$ samples was measured. In contrast to cobalt doping, the aluminium ions substitute for non-magnetic zinc. Consequently it is possible to affect both the magnetic structure and conduction band simultaneously through cobalt doping, or it is possible to affect only the conduction band through aluminum doping. Figure 5.6 presents zero field $\chi$ vs. $T$ curves for several concentrations of aluminum ions. The magnetic transition temperature is suppressed with increasing aluminum concentration in a manner similar to the temperature suppression seen in the cobalt doped case. The magnitude of the change in $\chi$ due to ordering is much larger for the aluminum doped case than for equivalent electron doping through cobalt. Figure 5.7 summarizes the effect on $T_c$ and $\Delta\chi$ for both cobalt and aluminum doping by plotting both quantities against extra electron number. The transition temperature is insensitive to the nature of the doping, being only dependent on the electron number. The change in $\chi$ at through the ordering is greatly enhanced with aluminum doping over equivalent cobalt doping.

As shown in Fig. 5.8, $\chi$ vs. $T$ for the lowest aluminum doping studied reveals a small dip near $T = 40$ K. Application of a static field does not change the temperature of this dip appreciably. However, by applying a field of 0.4 kOe the dip is suppressed. Such a dip in $\chi$ is not seen in other aluminum dopings. All other aluminum concentrations studied have $\chi$–$T$ curves similar to pure GdFe$_2$Zn$_{20}$, the main difference being the magnetic transition is shifted lower in temperature. The absence of additional features associated with local moment magnetism suggests that the effect of aluminum doping is not equivalent to that of cobalt
doping. Cobalt substitution directly affects the magnetic sublattice while aluminum doping only affects the conduction band.

The additional dip in $\chi$ for the low Al concentration may be due to one of several factors. It is possible that within a single sample, the aluminum concentration is not uniform. In this case regions within the sample will have different ordering temperatures owing to different local aluminum concentrations. Given the fairly steep slope of the $T_C$ vs. electron number curve seen in Fig. 5.7 a small variation in aluminum concentration can lead to a significant change in $T_C$. This is consistent with the observation that for increasing aluminum concentration the change in $\chi$ through $T_C$ increases. As $\chi$ from a high $T_C$ region is decreasing, the susceptibility from a lower $T_C$ region is increasing to a greater value. The overlap of these two procedures produces the observed dip. Any other explanation posited at this point would be speculation.
Figure 5.7 Change in $\chi$ through ordering (a) and change in magnetic transition temperature (b) vs. extra electron number. Solid symbols represent aluminum doping and hollow symbols represent cobalt doping.
Figure 5.8 $\chi$ vs. $T$ in applied DC fields for the four Al doped samples studied. Only the 0.5% and 4.9% Al dopings show well-defined additional features. Numbers next to each trace indicate the applied field in kOe.
5.3.4 Discussion

Complete replacement of cobalt for iron changes the ferromagnetic ordering of the gadolinium moments to antiferromagnetic. Based on the TDR data presented here, it seems that the transition is not smooth, with the ferromagnetic state persisting to high concentrations of cobalt. These findings are consistent with static measurements on the same compounds Jia et al. (2008). While high field, static measurements show that conduction band spin fluctuations are smoothly suppressed with increasing cobalt concentration Jia et al. (2007), the low field, rf data presented here suggest that considerable fluctuations persist up to at least 50% cobalt substitution. This should not be too surprising as there is little reason to suppose that the low field, dynamic response of material should be equivalent to the high field, static response.

Based on the evidence provided by rf susceptibility, it seems ferromagnetic order persists up to at least 75% cobalt substitution and 5% aluminium substitution. This conclusion is supported by the observed increase in $\chi$ below the magnetic ordering temperature seen in all ordered compounds except for GdCo$_2$Zn$_{20}$. The true nature of the magnetic order of the gadolinium moments in the compounds Gd(Fe$_x$Co$_{1-x}$)$_2$Zn$_{20}$ and GdFe$_2$(Zn$_y$Al$_{1-y}$)$_{20}$ is still open, however. Neutron scattering would normally be the ideal technique for determining this conclusively, but the small scattering cross-section for a natural distribution of Gd isotopes presents a particularly difficult obstacle. It is possible that magnetic x-ray scattering would provide information regarding how the magnetic structure evolves from ferro- to antiferromagnetic with increasing cobalt concentration. Magnetic x-ray scattering could also allow for a determination of the magnetic order in GdFe$_2$(Zn$_y$Al$_{1-y}$)$_{20}$ as the compound GdFe$_2$Al$_{20}$ does not exist.

5.4 Summary

Nine different chemical dopings on the mixed local moment/itinerant ferromagnet GdFe$_2$Zn$_{20}$ as well as GdCo$_2$Zn$_{20}$, YFe$_2$Zn$_{20}$, and YCo$_2$Zn$_{20}$ have been studied via rf susceptibility. The observed difference in the measured susceptibilities of YFe$_2$Zn$_{20}$ and YCo$_2$Zn$_{20}$ supports previous
conclusions that the Fe containing compound exhibits dramatic Stoner enhancement of the conduction band while the Co containing compound does not. The data on GdCo$_2$Zn$_{20}$ strongly support the conclusion that this compound orders antiferromagnetically at $T_N \approx 5.7$ K. Looking across both cobalt and aluminum dopings in GdFe$_2$Zn$_{20}$, the data show that increasing the valence electron population decreases the magnetic transition temperature and increases the change in $\chi$ through ordering. While the change in ordering temperature is independent of the nature of the electron doping, dopants which affect the magnetic iron site have a smaller effect on the change in $\chi$ than dopants on the non–magnetic zinc site. Whereas previous high field static results show that the Stoner enhancement of the magnetic susceptibility in the conduction band is gradually reduced, the low field radio–frequency results show that band fluctuations in the ordered state persist through at least 75% cobalt doping. These data suggest that the transition from ferromagnetic GdFe$_2$Zn$_{20}$ to antiferromagnetic GdCo$_2$Zn$_{20}$ does not proceed gradually. Rather an abrupt change in magnetic order apparently occurs with complete replacement of cobalt for iron.
CHAPTER 6. Thermal Response of Materials to the rf Probe Field

6.1 Introduction

As was stated in Ch. 1, the energy scales associated with the rf excitation field are very small – both the amplitude and the frequency contributions being $\leq 1$ mK in thermal equivalent units. However, in the cobalt doped GdFe$_2$Zn$_{20}$ samples it was noticed, quite by accident, that at base temperature as the magnetic field was swept up, the temperature of the sample dropped by approximately 100 mK. This temperature shift precisely correlates to the susceptibility of the sample, as shown in the blue curve of Fig. 6.1. This behavior was seen in the aluminum doped samples as well. From Fig. 6.2, where the temperature of an aluminum doped sample is plotted versus time as the rf field is turned on and off, it is evident that this effect is related to the presence of the rf excitation field. Given the obvious dependence of sample temperature on (a) the magnitude of the susceptibility and (b) the presence of the rf excitation field it was decided to try pin down the specific source of this effect. There are two possibilities.

First, the thermal effect (TE) could be associated with the power dissipated by the shielding currents induced in the skin-depth layer. Jackson (1998) shows that the time averaged power per volume associated with this effect is

$$P_{res} = \mu \pi f H_0^2 e^{-2z/\delta}.$$  \hspace{1cm} (6.1)

$H_0$ is the magnitude of the rf field, $f$ is the frequency of oscillation, $\mu$ is the magnetic permeability of the sample, and $\delta$ is the skin depth. $z$ represents the depth to which the oscillating field penetrates the sample. In the case of a long thin rod with the excitation field parallel to the long axis, the power dissipated per length is proportional to $\mu \rho f$. For a sphere, after
integrating by parts and assuming that the power density dissipated follows the form of Eq. 6.1 throughout predicts that the total power dissipated should be

\[ P^T = \frac{1}{2} A_s H_0^2 \sqrt{\pi \rho \mu_0}. \]  

(6.2)

In the above, \( A_s \) is the surface area of the sphere. An important prediction is that the power dissipated should vary like the square of the amplitude of the rf field and the square root of the magnetic permeability. As the dc field is increased the AC permeability drops, and the power dissipated drops. If we assume the magnetic permeability is inversely proportional to the applied field, then the power dissipated should increase in as the field is lowered, so this is a feasible scenario.

The second possibility is that the remagnetization of the magnetic moments in response to the rf field has a large decrease in entropy associated with it. The magnetic moments release this entropy to the lattice, resulting in an effective heating of the sample. As the dc field is increased, the ac susceptibility decreases and the remagnetization process is inhibited. This leads to a drop in entropy released to the lattice and a decrease in the heating. Invoking this mechanism requires considerable coupling between the spins and the lattice. It also requires the spins to have time to relax before the rf field changes direction. Samples with a large magnetic susceptibility at a given frequency satisfy this requirement. In this scenario the rate of change of entropy should be directly proportional to the frequency of the rf field, therefore the change in temperature should also be directly proportional to the frequency. The entropy should also be directly proportional to the magnitude of the rf field. Finally, the change in entropy (and power dissipated) should vary like \( 1/H_{dc} \). It can be expected that the temperature would vary like \( 1/H_{dc} \) as well.

The true test, then, for which mechanism is responsible for the heating is a frequency resolved measurement coupled with a varying rf amplitude. A slightly simpler test is to take a metal with no magnetic order and turn the rf excitation on and off to see if there is an effect on the temperature. Further, an insulating ferromagnet with a field dependent susceptibility will allow one to discriminate if the magnetic moments do play a direct role in the observed TE or
if the effect seen in the doped GdFe$_2$Zn$_{20}$ samples is due only to the effect of the permeability on the skin depth.

Figure 6.1  Magnetic field (solid line, left axis), sample temperature (filled circles, right axis), and magnetic susceptibility (half-filled pentagons, far right axis) vs. time for Gd(Fe$_{0.5}$Co$_{0.5}$)$_2$Zn$_{20}$. The correlation between the sample temperature and susceptibility is clear. Vertical bars near 1250 seconds denote the time period where the field was held at a non-zero, constant value.

Regardless of the source of the power (whether magneto-caloric or skin depth heating), the data on the doped GdFe$_2$Zn$_{20}$ systems demonstrate that the magnetic permeability is a key player. Further, for the TE to be observable the material must have a low heat capacity, $C$. If $C$ is large then the extra heat deposited into the system will go to changing the entropy rather than the temperature. Therefore, the effect should not be visible at higher temperatures. Another consideration is the proximity to a second order phase change. If the sample in question undergoes a para- to ferromagnetic phase change close to the measurement temperature, the heat capacity of the sample will be large and the magnitude of the TE is expected to be small. The final consideration is the size of the sample relative to the sample holder. If the sample is small it may not generate enough heat to measurably affect the sapphire and heater block
Figure 6.2 Sample temperature (left axis, solid symbols) and TDR temperature (right axis, open symbols) vs. time for 1% Al doping in GdFe$_2$Zn$_{20}$. Initially the rf excitation field was off. At approximately 1 minute the circuit was set resonating and the temperature was allowed to reach a steady state. The rf field was turned off again at 4 minutes, and the temperature relaxed to the time=0 value.
used in this experiment. In this sense, a better way to perform the experiment is to mount the sample directly to a thermally isolated thermometer and then apply the rf and dc fields. Still, it is evident that the TE discussed herein is measurable in some materials with the current equipment.

6.2 Experimental Details

Six materials were chosen for this experiment in an attempt to unambiguously identify the source of the TE: GdFe$_2$(Zn$_{0.979}$Al$_{0.021}$)$_{20}$, CeVSb$_3$, YTiO$_3$, GdPtIn, YFe$_2$Zn$_{20}$ and Cu. The first is seen to have a large and strongly field dependent $\chi$ at low temperatures. Further, it is believed to have a band magnetism component. CeVSb$_3$ is a metallic local moment ferromagnet with almost zero low temperature field dependence in $\chi$. Field dependent $\chi$ measurements suggest there is an aspect of the magnetism with considerable fluctuation. YTiO$_3$ is an insulating ferromagnet, but due to orbital ordering, the susceptibility remains large at low temperatures. It also has a similar field dependence in $\chi$ when compared to an itinerant compound for low temperatures. If the TE is related to the remagnetization, then the YTiO$_3$ might be expected to show it as well. If, however, it is only related to the joule heating from the shielding currents the Cu sample will show the effect. GdPtIn is a local moment ferromagnet, and the field dependent data suggests that it is pure local with little or no band enhancement. YFe$_2$Zn$_{20}$ is the non-magnetically ordered parent compound of GdFe$_2$Zn$_{20}$. It exhibits a large Stoner enhancement of its conduction band as discussed in Ch. 5. All samples were approximately 0.75 mm$^3$ in volume. With the exception of copper, all samples were single crystals. The copper sample was cut with a shear from a plate purchased from McMaster-Carr. This original purpose of the plate was to build a stage on which the $^4$He circuit was mounted. The cut piece of copper was washed in ethanol and acetone separately to remove any residual grease and/or oil from the cutting process. After a rinse in distilled water, the sample was etched with a 1:1 mixture of nitric acid and distilled water three times in an attempt to remove any surface impurities resulting from the cutting. After each etching, the sample was washed thoroughly in distilled water. When magnetic order was present, the magnetic easy axis was
aligned with the rf field.

6.3 Results and Discussion

The TE observed in the doped GdFe$_2$Zn$_{20}$ is not seen in any serious or conclusive way in Cu, YTiO$_3$, or GdPtIn. (Figs. 6.3, 6.4, and 6.5). Based solely on the energy considerations from Ch. 1 the size of the temperature shift seen in Cu is consistent with expectations given the relatively low permeability expected for this material. Further, the weak effect seen in the YTiO$_3$ suggests that the TE is not just from remagnetization processes. This is a much weaker conclusion, though, because it is difficult to estimate the absolute value of the moment change from the rf field due to a lack of knowledge of the precise value of the rf amplitude. However, this amplitude, and the subsequent moment change, should be quite small.

Figure 6.3 Circuit, 1-K pot, and sample temperature vs. time for a copper sample as the rf excitation field was cycled on and off. At time=0 the rf field was on. From a-e the rf field cycled between on, off, on, off, and on. Initial tests suggested the effect was small, so to mitigate any possible change in heat load due to the changing power dissipated in the circuit itself, the bias voltage on the diode was changed very slowly.
Figure 6.4  Response of the temperature of YTiO$_3$ with the rf field cycled between on-off-on (left axis, solid symbols) and the TDR temperature (right axis, open symbols). The effect is quite small, even with the heat pulse from rapidly changing the bias on the circuit.
Figure 6.5  Temperatures of GdPtIn (left axis, solid squares) and the circuit (right axis, open circles) vs. time as the bias voltage was increased. At the time marked ‘a’ the circuit began resonating. At ‘b’ the resonance switched off due to overbiasing.
That the effect is not connected with magnetic order is evident from YFe$_2$Zn$_{20}$. The heating effect is seen quite obviously in Fig. 6.6. Cycling the rf field on and off induces a 20 mK temperature change. This is somewhat smaller than that seen in the doped GdFe$_2$Zn$_{20}$, however it is substantially larger than what is seen in either Cu, YTiO$_3$ and GdPtIn.

![Figure 6.6 Sample temperature vs. time for YFe$_2$Zn$_{20}$ as the rf field was cycled on and off.](image)

The results of CeV$_3$Sb$_3$ are more interesting. Even though the compound exhibits strong local moment behavior and the low temperature susceptibility is not strongly field dependent, the effect on temperature of the rf field is obvious. This suggests that the TE discussed herein is due to the presence of ferromagnetic order in a metal.

Figure 6.7 presents the temperature of the sample versus time as the bias voltage is adjusted. Initially the rf field was off due to under biasing the circuit. The peak at ‘a’ indicates the resonance turned on. The bias was then reduced to bring it to a minimum value. Biasing was increased in approximately 100 mV steps until the resonance turned off at the negative peak ‘b.’ A frequency dependent measurement was attempted for this material over a very narrow window. By changing the bias voltage on the tunnel diode it is possible to change the resonant
Figure 6.7 Sample temperature for a 1 mm$^3$ single crystal of CeVSb$_3$ vs. time as the bias voltage is adjusted. The arrows labeled 1 and 2 are for increasing and decreasing bias voltages, respectively. The rf field was off at time=0.
frequency by a small amount. Even with this small change in $f$, there is a correlation between $f$ and $\Delta T$, as shown in Fig. 6.8. It is not strictly linear in $f$ nor is it even monotonic. Such non-monotonicity can be accounted for by realizing that as the bias point moves along the $I-V$ curve (Fig. 1.2) the amplitude of the rf field also changes. The rf amplitude might be expected to be very nearly constant over most of the range of suitable bias values. At the extremes the absolute value of the slope of the $I-V$ curve decreases. If the voltage oscillation about the bias point is of fixed amplitude for all bias points, then for lower slopes a smaller $\Delta I$ results. It is this change in the passed current that accounts for the amplitude of the radio frequency field. Therefore, at the extreme bias voltages, the amplitude of the rf field may be expected to decrease. Through the middle of the bias voltages, though, one is tempted to assume the rf field maintains a fixed peak to peak amplitude.

Figure 6.8  Sample temperature vs. resonant frequency for CeVSb$_3$. The arrow indicates the direction of decreasing bias voltage.

However, this appears not to be the case. The sample temperature is directly proportional to the bias voltage, only becoming non-monotonic at the highest bias values (Fig. 6.9). These points on the temperature downturn correspond to resonances that were especially unstable, changing as much as 500 Hz in a matter of seconds, a consequence of being marginally biased.
It might be argued that since the bias voltage is increasing more power is being dissipated in the other circuit elements as well as the coil itself. This argument is laid to rest by noting that once the resonance is shifted off, either by over or under biasing, the temperature of the sample drops (Fig. 6.7). Referring to Fig. 1.2, the curvature of the TD $I-V$ plot is much greater near the peak current when compared to the valley at higher bias voltages. This can account for the continued monotonic behavior down to the lowest resonating biases as the crossover from negative to positive slope occurs over a much smaller voltage window.

![Figure 6.9](image-url)  
**Figure 6.9** Sample temperature (left axis, filled circles) and resonant frequency (right axis, hollow squares) vs. bias voltage for CeVSb$_3$. The lower and upper voltage points denote the resonance window.

### 6.4 Conclusions

Magnetically soft, highly permeable metals show a pronounced thermal effect in response to an rf field. The ferromagnetic insulator YTiO$_3$ does not manifest this effect even though it is a highly polarizable material at low temperatures. This effect is due to the Joule heating from the screening of the rf field by the conduction band electrons. A comparison of the heat dissipated in copper and YFe$_2$Zn$_{20}$ as the rf field is cycled on and off shows that the
conduction band must have a high polarizability for the effect to be observable. Given the very small amplitude of the rf field ($\leq 6$ mOe, estimated) the polarizability requirement is not too surprising.

All these observations taken together suggest that for the rf heating to be manifest in the TDR measurements the conduction band electrons must have a fairly large polarizability. Coupling these data with the field swept data on both CeVSb$_3$ and GdPtIn at base temperature suggest that CeVSb$_3$ has a highly polarizable conduction band, even though the magnetism is strongly localized on the cerium sites. In a manner similar to the cobalt and aluminum doped GdFe$_2$Zn$_{20}$ the conduction band may be polarizable in low fields, but show saturation in somewhat larger fields. Therefore, dc measurements may mask the low field, dynamic response of the materials under consideration. Even though the measured Stoner enhancement is low, the materials are still dynamically very active for sufficiently low $H$.

Given the requirement of passive heating to observe this effect coupled with the varying heat link and base temperature from run to run, it is difficult to make any systematic comparison between different samples. Still, the fortuitous discovery of the rf heating may offer another avenue to explore the nature of the differences between band and local moment magnetism. An experimental system optimized to passively heat the sample to a certain temperature would allow for a better estimate of the power dissipated in a given sample. From a series of such measurements on differently sized samples it may be possible to determine the amplitude of the rf field which would allow for a second method to determine the magnetic permeability in a sample. Such a study would be very valuable for determining how band magnetism behaves.
CHAPTER 7. Conclusion and Future Directions

Sensitive measurements of the rf susceptibility have been shown to be of use in many areas in magnetically active samples. In local moment ferromagnets such measurements have uncovered the existence of an internal field that is apparently related to the exchange coupling. This field is frequency dependent and does have an effect on critical scaling analysis. Further, it has been demonstrated that the conditions leading to magnetic anisotropy do exist up to and above the Curie temperature. The behavior of $\chi$ near $T_C$ has been shown to be unrelated to the formation of domains, indicating that the peak seen in LFM’s is, in fact related to the phase transition itself. The differences between local moment and itinerant systems have been demonstrated. Attempts at disentangling the resistive screening and the magnetic spin susceptibility contributions to the measured $\chi$ were made, with some promising results for truly understanding such effects. Field dependent data strongly suggests that the unpolarized fraction of the conduction band is what is probed by the TDR. A simple model based on this assumption has been developed, and it reproduces the measured data in low, non-zero, applied fields reasonably well. It has also been shown that Joule heating in metals with a highly susceptible conduction band occurs at megahertz frequencies. This heating effect may prove useful in determining how the conduction band polarizability changes with applied fields and/or doping as in the series fo doped GdFe$_2$Zn$_{20}$. Finally, the magnetoelectric effect has been tentatively identified in certain multiferrioc compounds.

In the course of this work, the main development to occur for the TDR as an instrument was pushing it into the high temperature realm. Such measurements had been performed prior to this work, but not pursued in any manner, serious or otherwise. Other abortive attempts were made to extend the capabilities of the TDR in several directions; frequency dependency
and dielectric constant measurements being the main two.

The TDR can be modified to study other types of materials as well as other dependencies. An obvious extension of this work is to examine frequency dependent behavior in ferromagnets. The two data points in Fe$_{1/4}$TaS$_2$ suggest that for some materials, at least, this window in $f$ is just right. Further, the scaling behavior seen in the local moment systems studied here may actually be a finite frequency effect. The analysis of the peaks in $\chi$ seen in CeAgSb$_2$, YTiO$_3$ and GdPtIn (Ch. 3) suggest that for some samples the ordering may be affected by this tens of MHz regime. The only way to truly sort this out is to perform the measurements over 1-1.5 orders of magnitude in frequency. The issues with constructing such a setup are manifold, however.

First, the condition for resonance is that the impedance of the tank circuit be less than or equal to the impedance of the tunnel diode. This can only be met for a fairly small range of inductances and capacities. This can be overcome by simultaneously varying the inductance and the capacitance. The obstacle here is that for stability the components must be held at a constant temperature and in fairly close proximity to the tank coil. By extension, the components must be at low temperature. It is very difficult to adjust both $L$ and $C$ at or near base temperature without introducing extra heat and noise in the resonance. Aslam and Weyhmann (1973) suggest using varactor diodes. These are diodes that are designed to have variable capacitance as the voltage drop across them varies. The drawback is that below about 100 K the change in capacitance with applied voltage becomes almost zero. Further, since the resonant frequency depends on the square root of $LC$, a small change in $f$ requires a fairly large change in the tank circuit parameters (one order of magnitude change in $f$ requires two orders change in $LC$). Still, it is possible to construct a set of circuits that span the frequency range from 1 MHz to 1 GHz in discrete steps. The upper bound on the switching speed for the tunnel diode is on the order of 5 GHz, and this low GHz range has been obtained by other groups [Martin et al. (2005)]. The major drawback to this approach is that the filling factor for each sample will likely change as the coil properties will have to change to accommodate the varying capacitor. One might suggest going to differently sized samples to keep the filling
factor constant. What may happen then is in certain materials the smaller samples may not
be skin-depth limited while the larger may. Even within the skin depth limited regime, as
the frequency varies, the skin depth varies as well. Again, the variation in $\delta$ is $1/\sqrt{f}$, so a
large change in frequency is required to substantially change the skin depth. Regardless of the
magnitude, it must be remembered that the change is present.

The key feature such an array of TDR’s must have is a common tank coil. It is not
unreasonable to consider varying the tap coil inductance, as it contributes to the resonant
frequency. This would allow the tank coil to remain constant while simultaneously varying
the total $L$ keeping the circuit properly tuned on resonance. This variation in the tap coil
inductance must be achieved without recourse to physically changing the coil. Resoldering
even one connection can change the resonant frequency by 5-10%. Ideas such as these are
not likely to occur to new graduate students pursuing research with the TDR. This is because
experience with what does and does not work is needed in order to modify the apparatus.
Building on past mistakes, though, should allow for such research to be attempted.

A second direction the TDR can be taken is into the pressure realm. Other groups have
successfully employed the TDR to make measurements of $\lambda$ in superconductors under hydro-
static pressure. In this case, the tank coil would likely need to be rewound for each experiment.
There are relatively few obstacles to implementing this measurement. What is required is the
knowledge of how to apply the pressure at low temperatures and how to feed the rf signal into
the cell.

Since there is obvious orientational dependence of the response of magnetically ordered
samples, a transverse $\chi$ apparatus, where the static and rf fields are perpendicular to one
another, would be quite nice. This is practically a nuclear magnetic resonance set up, however
it should allow for a direct determination of the magnetocrystalline anisotropy constants by
taking field swept data at different temperatures. The natural motion of a moment in an applied
field is precession about the field direction. The precession has a characteristic frequency which
depends on the applied field. In addition, it should depend on the anisotropy in the sample. If
the TDR frequency can match the precession frequency for some attainable field, there should
be a maximum in measured $\chi$. By rotating the sample so that susceptibility is measured along its principal axes, it should be possible to reconstruct the anisotropy constants.

A most useful measurement would be to adapt the TDR back to VanDegrift’s setup and measure $\epsilon$ as functions of $T$, $H$, and $E$. The obvious immediate application of such a system is to the multiferroics (Ch. C) in an attempt to clarify the mutual effect of the coexisting orders. This could possibly be useful in examining systems that exhibit orbital ordering, as in $\text{YTiO}_3$ or $\text{Ba}_2\text{NaOsO}_6$ as well. Another possibility that can be explored with the capacitor as the active element is the effect of the rf electric field on both ferromagnets and superconductors.

From the high temperature setup, it would be interesting to examine the magnetic susceptibility of a metal through the melting point. This might be particularly interesting for magnetically active samples, either intrinsically or through a dilute doping of local moments or an embedding of superparamagnetic particles in a low-melting point matrix, like lead or tin. For the single ion case, such an experiment would work best on doped single crystals. This experiment would be difficult to perform because of the need to keep the sample in the vacuum. It might be possible to place the entire sample in a sealed quartz ampule to prevent coating the interior of the vacuum chamber.

In order to limit the background induced by the bias field, a detailed study of different types of wire for the rf coil would be useful. Since most copper magnet wire is fairly impure, there can be a significant magnetoresistance in the coil. This is on top of the intrinsic response of the copper itself. Using a wire with a larger absolute resistance, but with a smaller magnetic response could significantly limit the drift introduced by the dc field. It might even be worthwhile to attempt to wind a coil from superconducting magnet wire, like NbTi. Given the very low current driven through the coil, such a wire is unlikely to be driven normal by the applied field, unless it heats significantly.

The TDR circuit could also be used in lieu of a capacitance bridge to construct a dilatometer or a torque magnetometer. In this configuration, the tank capacitor either would have placed in parallel or replaced entirely with a parallel plate capacitor. One of the plates would be flexible or mounted on an insulating track of some sort. The sample under consideration
would be connected to the moving plate. For the dilatometer, the other end of the sample would have to be mounted to a stationary surface, similar in construction to other dilatometers [Schmiedeshoff et al. (2006)]. For the magnetometer it would be most useful to place the sample in a gradient field so that zero field measurements of magnetic moment could be taken. In either case, changes in the sample properties would be translated to changes in the resonant frequency via the capacitance. The problems with calibration associated with this setup should be no different than those encountered in standard techniques.

Continuing to pursue this particular line of research, i.e. local moment vs. itinerant ferromagnetism, some of the other weak itinerant magnets would be useful to examine. Ni$_3$Al is considered an itinerant magnet while Ni$_3$Ga is not [Aguayo et al. (2004)] due to strong critical spin fluctuations. It might be fruitful to try to substitute Ga for Al in the crystal and push the sample across the magnetic border. Another system that would be interesting to look at is CoVSb. Band structure calculations suggest this material is a half-metal for certain atomic configurations. However, neutron scattering data on powder samples suggests it is a weak itinerant rather than half-metallic [Heyne et al. (2005)].

The TDR is an extremely versatile and powerful technique. The utility of the device has only just begun to be explored. It is hoped that through the years it is applied more fully to explore more materials and effects and that the knowledge base be expanded.
APPENDIX A. Design and Materials Considerations for the TDR

Three different TDRs were used to collect data for this work. The first is mounted on a closed cycle $^3$He cryostat with a temperature range from 0.5-100 K operating at a frequency of 13 MHz. To minimize any drifts in the signal due to varying circuit properties, the circuit temperature is stabilized at 5 K. The actual temperature used is not as important as the fact that the temperature is held stable. This resonator had been constructed previously and was working in a nearly optimal manner. The sample is mounted on a sapphire rod approximately 25 mm long and 1 mm in diameter with a small amount of Apezion low temperature grease. The opposite end of the sapphire is mounted in a copper block (approximately 4 mm in diameter and 10 mm long) with Stycast 1266 epoxy. Wound around the copper block is a length of doubled over and twisted nichrome wire (room temperature resistance $\approx 75 \, \Omega$) which acts as a heater. A Cernox thermometer (Lakeshore SD package) is glued to a flat milled on the heater block between the heater coil and the sapphire with a thin layer of GE-varnish. The sample end of the sapphire is inserted into the coil of the LC tank circuit. The entire apparatus (circuit and sample) are placed in a vacuum can that is pumped to a typical pressure of $10^{-5}$-$10^{-6}$ torr. This pressure is sufficiently low to allow for separate control of the sample and circuit temperatures.

At the temperatures of interest ($T \leq 100$K) the maximum temperature gradient between the sample and the thermometer is estimated to be less than 50 mK. This estimate is derived from a comparison of Curie temperatures of several samples as determined from the TDR and published values. This gradient grows in absolute value as the temperature grows. At low temperatures ($T \leq 30$ K) the gradient is less than 10 mK which can be far overshadowed by differences in thermometer calibrations. The major drawback of the $^3$He system is that
the circuit elements, in particular the tunnel diode, are placed in the magnetic field. This introduces a sizeable field induced background due to the field dependent properties of the diode. Fortunately, this background is very reproducible within a single run. Further, if one can reasonably assume that the only shift in resonance at high temperatures is due to the circuit itself, then the temperature swept data can be shifted so that high temperature portions overlap. This may or may not be a reasonable assumption. It is expected that for the fields of interest in this work ($H \leq 10$ kOe, often $H \leq 2.5$ kOe) this assumption should be fairly valid.

The other two systems used were constructed for this work. To be sure, they were modeled on the $^3$He system, however it was possible to make certain modifications to permit collection of field swept data at constant temperature and allow access to higher temperatures. The first constructed system is mounted on a $^4$He cryostat with a sample temperature range of 2-300 K operating at a frequency of 28 MHz. Here the circuit temperature is stabilized at 7.5 K. A major difference between the $^3$He and $^4$He systems is that the circuit in the former is mounted below the sample while it is above the sample in the latter. There is a coaxial cable that transmits the rf signal from the tank circuit to the rest of the low temperature elements.

The sample holder in the $^4$He system is modeled very closely on the $^3$He sample holder. The main difference is that the sapphire is approximately 35 mm long and 2 mm in diameter. This allows for larger samples to be studied, but requires more care in heating the sample. One way to compensate for the larger overall sapphire mass is to use a larger heater block, which was employed here. The rationale is that the heat capacity of the heater block needs to be large enough that the temperature rises slowly enough to keep both ends of the sapphire in near thermal equilibrium. A check on this condition is to sweep the temperature up and down through a second order phase transition. If there is significant thermal lag, then there will be artificial hysteresis in the temperature sweeps. If such hysteresis is present, a slower temperature ramp rate can be used. Exceptionally high temperatures ($T \geq 250$ K) pose additional problems. Even by ramping up to room temperature over the course of 2 hours ($\approx 2.5$ K/min) thermal lag is still observed. Ramping much slower than this is not reasonable
in the $^4$He system as constructed because the 1K pot on which the sample and superconducting magnet are mounted is not able to maintain a low enough temperature to prevent the magnet from transitioning to the normal state. It does not have enough cooling power. This undesirable situation results in a loss of magnetic field and a wasted run. Therefore, temperatures near 250 K and higher are to be considered approximate and no forceful identification of transition temperatures should be made. A newer cryostat with similar design was recently purchased, and it has a larger 1K pot. This new version should provide enough cooling power to keep a conductively cooled magnet in the superconducting state even while heating the sample up to and above room temperature. Also, the sample holder could be redesigned to allow for these higher temperatures.

The long sapphire, which is the source of many thermal problems, is needed because a superconducting magnet was made in house to mount inside the vacuum can for this system. This allows for the application of magnetic field on the sample while keeping the diode in a relatively field-free region. Therefore, the $^4$He system permits field swept data to be collected. Further, the $^4$He system has an \textit{in situ} extraction mechanism that allows for the removal of the sample from the coil at base temperature. This permits an estimate of the absolute value of the susceptibility. Such an estimate is useful in making comparisons of the band component of the ferromagnetism in cobalt and aluminum doped GdFe$_2$Zn$_{20}$ presented herein. This also allows for an estimate of the absolute value of the penetration depth in superconductors, which is necessary for a determination of the superfluid density [Prozorov et al. (2000), Prozorov and Giannetta (2006)].

The third system is a high temperature version christened the “Inferno.” The circuit temperature is allowed to float near room temperature. This system allows access to temperatures as high as 800 K, and operates at a frequency of approximately 36 MHz. The sample holder is a single copper rod (100 mm long and 5 mm initial diameter) with one end turned down to a diameter of approximately 3 mm. A flat surface is milled on one side of the turned diameter. While the $^3$He and $^4$He systems are constructed with a vertical geometry, the Inferno was finally set up horizontally. Samples are secured to the stage with sliver paste which is allowed
to cure for two hours at room temperature before heat curing with the sample holder itself. Heat is applied through two filaments from 100 W incandescent bulbs wired in parallel and wrapped around the larger diameter of the copper rod. The heater filaments are secured with Resbond 940 LE potting compound. This is a two part silica based adhesive commonly found sealing the bases of incandescent bulbs. It is rated to 1370°C, and designed to very nearly match the thermal expansion of fused silica. Sample temperature is monitored with a platinum resistance thermometer (Lakeshore PT-103) mounted in groove milled in the copper rod. To permit changes in the thermometry, should such need arise, the thermometer sits in a copper sleeve that is attached to the rod with the same potting compound used to adhere the heater. The vacuum chamber for this system is a KF-25 nipple 30 cm long. The coil is mounted in a hollow drilled out of one end of a 6.35 mm diameter copper rod. Both the coil and the sample holder are in the vacuum chamber and the circuit is in air. A small resistive magnet is wound directly on the vacuum chamber allowing the application of a dc bias field.

An obvious improvement to the Inferno is to actively stabilize the circuit temperature. A passive stabilization is done by gluing the circuit board to an aluminum table (61×61×2 cm³ top plate). The drift introduced by not stabilizing the circuit temperature is overwhelmed by the drift caused by the sample holder. For the low temperature versions, sapphire is used as the sample mounting surface because it is a diamagnetic (in the absence of impurities) insulator but has high thermal conductivity at low temperature. The thermal conductivity drops as temperature increases because it is mediated by phonons. Using a metal allows the thermal conductivity to stay fairly high because it can be mediated by the conduction electrons. The tradeoff is that the metal shows a changing ac susceptibility due to its changing resistance. Again, this background signal is largely reproducible. The irreproducible part likely comes from the thermal cycling of the coil.

The specifics of our systems are summarized in Table A.1.

Figure A.1 is a circuit diagram of the biasing supply and a block diagram of the room temperature electronics used in collecting the TDR data. This is a simplified version of the bias supply, as it omits an op-amp that may be used to further stabilize the voltage. However, with
Table A.1  TDR Specifics

<table>
<thead>
<tr>
<th>System</th>
<th>Coil Volume (mm³)</th>
<th>$f_{res}$ (MHz)</th>
<th>Temp. Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$He</td>
<td>31</td>
<td>14</td>
<td>0.5-100</td>
</tr>
<tr>
<td>$^4$He</td>
<td>33</td>
<td>28</td>
<td>2-300</td>
</tr>
<tr>
<td>Inferno</td>
<td>250</td>
<td>36</td>
<td>293-800</td>
</tr>
</tbody>
</table>

Figure A.1  Room temperature electronics for the tunnel diode.

such a circuit, it is possible to obtain the highest sensitivity as VanDegrift showed [VanDegrift (1975b)]. The 10 nF capacitors in conjunction with the 2 kΩ resistors act as low pass filters, shunting frequencies on the order of 50 kHz and greater to ground. If more stringent ac filtering is required, a π-filter (an inline inductor with each end capacitively connected to ground) can be used. A voltmeter can be employed to monitor the bias voltage being applied to the TDR. The 1 μF capacitor acts as a high pass filter, shunting the rf signal from the low temperature circuit to an amplifier. The amplified signal is fed into a mixer where it is subtracted from a fixed local oscillator frequency. The resulting mixed frequency is in the kHz band. This kHz signal is filtered and amplified before being sent to a counter and an oscilloscope. In principle the oscilloscope is not necessary, as the information is extracted from the frequency of the
oscillations. What the oscilloscope offers is the chance to observe the waveform and assure oneself that there are no or few harmonics mixed into the main signal. The actual instruments used in these experiments are listed in Table A.2.

Table A.2  Commercial electronics used in this work

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Use</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>MITEQ AU-1494</td>
<td>rf Amplifier</td>
<td>1-200 MHz, 58 dB</td>
</tr>
<tr>
<td>MiniCircuits ZX05-1-S+</td>
<td>Mixer</td>
<td>0.5-500 MHz input, 7dB drop</td>
</tr>
<tr>
<td>Agilent 33250A</td>
<td>Local Oscillator</td>
<td>0-80 MHz, 0.01-10 V</td>
</tr>
<tr>
<td>SRS 560</td>
<td>Filter &amp; Preamp</td>
<td>variable BP filter DC-1 MHz, up to $5 \times 10^4$ amplifier</td>
</tr>
<tr>
<td>Agilent 53131A</td>
<td>Counter</td>
<td>up to 225 MHz input frequency</td>
</tr>
<tr>
<td>Agilent 54622A</td>
<td>Oscilloscope</td>
<td>100 MHz dual channel</td>
</tr>
</tbody>
</table>
APPENDIX B. Shubnikov-de Haas Oscillations in Ce- & SmAgSb$_2$

Measurements of quantum oscillations in the resistivity, Shubnikov-de Haas (SdH) oscillations, is one of the primary techniques to study the geometry of the Fermi surface in metals. Electron transport depends on the density of states and the scattering rates, both of which are modulated by the Landau quantization. Within the standard theory [Shoenberg (1984)] for a three-dimensional Fermi surface the amplitude of the $r^{th}$ harmonic oscillatory part of the resistivity is given by

$$\alpha_r \propto m_c S_{extr} B^{1/2} \frac{1}{|S''_{extr}|^{1/2}} R_T(r) R_D(r) R_S(r)$$  \hspace{1cm} (B.1)

where $m_c$ is the cyclotron mass, $S_{extr}$ is the extremal cross section of the Fermi surface (FS) perpendicular to the applied field, $|S''_{extr}| = (\partial^2 S / \partial p_B^2)_{extr}$ is a measure of the FS curvature along $B$ at the extremal cross section, and the damping factors $R_T$, $R_D$, and $R_S$ are caused by finite temperature, scattering, and Zeeman splitting respectively. The corresponding fundamental frequency is

$$f = \frac{S_{extr}}{\hbar e}$$  \hspace{1cm} (B.2)

Such oscillations are generally difficult to measure in three-dimensional metals, especially if the metal is highly conducting. The problem is exacerbated for small crystals where attaching contacts is not an easy task. Further issues arise in materials with a small cyclotron mass, giving rise to a reduced amplitude of the SdH signal. The TDR allows for a contactless measurement of the resistivity and changes therein by probing the skin depth (Eqs. 1.1 and 1.17).

In large magnetic fields far from any possible ordering effects, where $\mu \approx 1$, the magnitude
of the skin depth at 13 MHz can be estimated by

\[ \delta[\mu m] = 15 \sqrt{\rho[\mu \Omega \text{ cm}]} \]  \hspace{1cm} (B.3)

For crystals with a typical size \( R = 500 \mu m \), the upper limit on the resistivity that the TDR used here can probe can be estimated by equating \( \delta = R \). This gives \( \rho_{\text{max}} \approx 1000 \mu \Omega \text{ cm} \). The lower bound on resistivity is reached when the skin depth becomes smaller than the mean free path, \( l \), and the local Ohm’s law is no longer valid. This is the anomalous skin effect. An estimate on this lower bound can be made using a Drude approximation where \( l \) is given by

\[ l = \frac{(3\pi^2)^{1/3} \hbar}{n^{2/3}e^2 \rho} \]  \hspace{1cm} (B.4)

\( n \) is the electron density and \( e \) is the electron charge. Combining equations 1.1 and B.4 one obtains

\[ \rho_{\text{min}} = \left( \frac{\mu f \pi^{7/3} \hbar^{2/3} e^2}{n^{4/3} e^4} \right)^{1/3} \approx 8.6 \times \left( \frac{\mu f}{n^{4/3}} \right)^{1/3}. \]  \hspace{1cm} (B.5)

For a typical nonmagnetic metal with \( n = 5 \times 10^{28} \text{ m}^{-3} \) and \( f = 10^7 \text{ Hz} \), \( \rho_{\text{min}} \approx 0.03 \mu \Omega \text{ cm} \). Therefore, a direct quantitative study of the contactless resistivity in small crystals in the range 0.03-1000 \( \mu \Omega \text{ cm} \) is possible. This range covers most metallic materials of interest.

In the regime of a highly conducting metal, the measured susceptibility is expressed by the linearized form of Eq. 1.17,

\[ 4\pi \chi = \frac{\mu \delta}{2R} - 1. \]  \hspace{1cm} (B.6)

Agreement between the resistivity in SmAgSb\(_2\) derived from skin depth and that measured via a direct 4-probe technique is very good, as seen in Fig. B.1.

Presented here is field dependent data at different temperatures from slab shaped samples of Ce- and SmAgSb\(_2\). Both crystals are tetragonal intermetallic compounds. CeAgSb\(_2\) orders ferromagnetically at 9.8 K, while SmAgSb\(_2\) orders antiferromagnetic ordering at 9.5 K. These materials, along with the other rare earth members of the family, has been studied before [Brylak et al. (1995), Sologub et al. (1995), Myers et al. (1999b), Myers et al. (1999a), Jobiliong
Figure B.1  Comparison of temperature dependent resistivity derived from skin depth (solid line) and 4-probe (hollow circles) in SmAgSb$_2$.  
Inset: Skin depth vs. temperature as measured by the TDR.
et al. (2005)]. Direct measurements of SdH oscillations have been reported previously [Myers et al. (1999a)].

Since the technique is best suited to measurements of changes in $\chi$ (and hence $\rho$) the insensitivity to the residual resistivity illustrates another advantage. The amplitude of the measured resistivity oscillations is on the order of a few nΩ cm (see Fig. B.3), while the absolute value of the background resistivity is on the order of 100's of nΩ cm (as determined by conventional 4-probe transport measurements). Resolving changes on the order of 1% or less of the background signal can be difficult using normal techniques. This is especially evident as the temperature of the samarium sample is raised. Thermal scattering decreases the amplitude of the oscillations (Eq. B.1). This is coupled with an increase in the resistivity of the sample. The net result is a greatly diminished signal to noise ratio. However, the TDR measurement detects high field oscillations up to 9.5 K.

The power spectra obtained from a Fourier transform of the oscillations is relatively simple for the cerium compound with only one major frequency evident. Conversely, the samarium compound exhibits many frequencies associated with the extremal Fermi surfaces as seen in Fig. B.5. The main peaks are identified by the Greek letters $\alpha$, $\beta$, and $\gamma'$. The hole orbit identified as $\gamma'$ was first observed with the TDR.
Figure B.2 Temperature variation of the resonant frequency oscillation amplitude in CeAgSb$_2$. 
Figure B.3  Temperature variation of the oscillation amplitude in SmAgSb$_2$. Note the scale of $\Delta \rho$. 
Figure B.4  Power spectrum of resistivity oscillations at three temperatures for CeAgSb$_2$. 
Figure B.5  Power spectrum of the resistivity oscillations at 0.5 K for SmAgSb$_2$. The peak at 0.89 MG derives from a newly observed hole orbit.
APPENDIX C. Multiferroic Compounds

Introduction

Recent years have seen a resurgence in the interest in magnetoelectric multiferroics (materials exhibiting simultaneous magnetic order and electric polarization) [Spaldin and Fiebig (2005)]. The possibility of controlling the magnetic subsystem via an electric field or vice versa could have significant implications for the field of information storage. Candidate materials that conclusively exhibit these properties are few in number, making detailed study of the physics involved rather difficult. One family of materials that is high on the list of potentials is the hexagonal rare earth system $R\text{MnO}_3$ ($R=$Ho-Yb).

The full rare earth series exists in either a hexagonal or an orthorhombic structure depending on the pressure and/or rare earth ion. The heavier, smaller rare earths (Ho-Lu) along with yttrium favor the hexagonal phase while the lighter and larger (La-Tb) tend toward the orthorhombic phase [Yakel et al. (1963)]. Normally, symmetry conditions would prevent the hexagonal phase from showing a linear magnetoelectric effect (ME), wherein an electric (magnetic) field can control the magnetic (electrical) properties of the system [Lottermoser et al. (2004)], however it has been demonstrated that hexagonal HoMnO$_3$ shows evidence of strong magnetodielectric coupling [Yen et al. (2005)].

An interesting aspect of HoMnO$_3$ is its rich $H - T$ phase diagram [Fiebig et al. (2002b) Lorenz et al. (2005)]. Frustration in the Mn sublattice has been cited as one reason for this richness. Fiebig et al. (2002b) claim that the other hexagonal $R\text{MnO}_3$ compounds with partially filled $4f$ shells exhibit phase diagrams comparable to HoMnO$_3$ as determined from second harmonic generation. That there are multiple phase transitions is presented by Fiebig et al. (2002a) and Fiebig et al. (2003). However, published magnetization, magnetic susceptibility,
and dielectric constant data [Yen et al. (2005)] seem to contradict this statement. It may be that the latter measurements lacked sufficient sensitivity to detect the phase changes. Fiebig et al. (2002a) label one of the phase transitions in ErMnO$_3$ as “hidden,” hinting at its aversion to detection. It has been speculated that the large Ho$^{3+}$ moment better couples to the Mn$^{3+}$ moments and may thus provide some explanation for the differences in diagram complexity and detectability of the transitions [Fiebig et al. (2002b)].

Unlike the other hexagonal members of this family, DyMnO$_3$ has received little attention. This member is usually encountered in the orthorhombic structure, but it can also be synthesized in the hexagonal [Kamegashira et al. (2004), Ivanov et al. (2006)]. Dy$^{3+}$ with an even larger free ion moment than Ho$^{3+}$ may be expected to manifest properties similar to holmium if the coupling between the Mn-3$d^4$ and $R - 4f^n$, where $n$ represents the filling of the $f$ shell, moments is driven mainly by the size of the moment. The $H - T$ phase diagram for the orthorhombic structure has been mapped [Kimura et al. (2005)], and the properties extensively studied [Goto et al. (2004), Laverdière et al. (2006), Feyerherm et al. (2006), Prokhnenko et al. (2007)]. Therefore, the dysprosium compound offers a stage on which the effects of structural differences and rare earth moment size on the magnetic order and any ME can be explored.

Single crystal samples of hexagonal Dy- and HoMnO$_3$ were grown via a floating zone method [Ivanov et al. (2006)]. Samples were first cut into plates with a wire saw and orientation was verified via Laue diffraction. From the oriented plates smaller pieces were cut with a blade for the resonator samples. The holmium sample was a planar right triangle with dimensions of $0.7 \times 0.7 \times 0.06$ mm$^3$ while the dysprosium sample was a rectangular plate with dimensions of $1 \times 0.75 \times 0.3$ mm$^3$. The smaller sample was mounted on one end of a 20 mm long by 1 mm diameter sapphire rod with low temperature grease. The opposite end of the sapphire was secured in a copper heater block where temperature was monitored with a negative temperature coefficient resistance thermometer. Sample and sapphire were then inserted into the coil of the $LC$ tank circuit of the TDR mounted on a $^3$He cryostat. The entire low temperature part of the setup was enclosed in a vacuum can permitting independent control of the circuit and sample temperatures. The cryostat was placed in the bore of a superconducting magnet. The
dc bias and rf excitation fields both were aligned parallel to the c-axis. All data was collected as temperature sweeps in constant field.

**Phase Diagrams for Hexagonal HoMnO$_3$ and DyMnO$_3$**

![Phase Diagrams](image)

Figure C.1  AC susceptibility of HoMnO$_3$ measured parallel to the c-axis in different dc magnetic fields. Curves are offset for clarity.

Figure C.1 presents the magnetic susceptibility versus temperature for HoMnO$_3$ in four applied dc fields. The zero field curve shows an obvious phase change near 4.5 K and a weaker feature near 40 K. Application of a modest field (2.5 kOe) does not appreciably change the temperature dependent susceptibility. As the dc field is further increased, more features of different types become evident. Each feature is associated with a change in the magnetic order of either the holmium or manganese spins or both.

Previous works have used an onset criterion for delineating phase boundaries in this material [Lorenz et al. (2005), Yen et al. (2005)]. Here a different set of criteria is used, as illustrated in Fig. C.2. When a well-defined peak is present, the temperature of that peak is taken as the critical temperature for the phase transition ($T_4$). In the absence of an obvious peak, linear extrapolation of the $\chi - T$ curves on either side of the transition is done ($T_1 - T_3$).
Figure C.2 35 kOe temperature sweep for HoMnO$_3$ along the $c$-axis with features associated with phase changes marked by $T_1 - T_5$.

The intersection of these extrapolated curves is taken as the critical temperature. Inflection points marking a change from an increasing to a decreasing slope ($T_5$) are also identified as being associated with changes in magnetic structure. The difference between these two sets of criteria do not affect the conclusions of this work.

Figure C.3 is the $H - T$ phase diagram for HoMnO$_3$ as determined via TDR measurements. For comparison the phase diagrams from Lorenz et al. (2005) and Yen et al. (2005) have been digitized and added. Figure C.4 is an expanded view of the low temperature region of Fig. C.3. The similarities between the TDR phase diagram and the published versions is striking. The difference in the high temperature lines is ascribed to differences in sample quality. What is intriguing about the low temperature region is that certain magnetic susceptibility points detected by the TDR more closely correspond to anomalies previously detected via dielectric constant measurements (bowties in Figs. C.3 and C.4). To be sure, not every feature seen via dielectric measurements is present in the TDR, but that may be due to selection criteria. It is evident, though, that the TDR is quite capable of detecting the many phase changes seen in HoMnO$_3$. 
Figure C.3  Phase diagram for HoMnO$_3$ measured along the c-axis. Solid circles are phase changes detected with the TDR. Open red triangles are defined phase transitions digitized from Lorenz et al. (2005). Blue bowties are anomalies in dielectric constant digitized from Yen et al. (2005). Lines are guides to the eye, and labeled phases follow the convention of Lorenz et al. (2005).

Figure C.4  Low temperature detail of the phase diagram show in Fig. C.3.
Fig. C.5 presents the $H - T$ phase diagram from HoMnO$_3$ with the dc and rf fields applied in the basal plane. No intermediate phase transition is observed as for the $c$ axis data. The high temperature transition evolve with field in a manner quite different from the perpendicular orientation, however comparison with Fig. C.7 shows that there are some similarities between DyMnO$_3$ and HoMnO$_3$ phase diagrams.

Figure C.5  Full phase diagram for HoMnO$_3$ measured in the basal plane.

Fig. C.6 presents $\chi$ versus $T$ data for hexagonal DyMnO$_3$ in five applied dc fields. The zero field similarity between the dysprosium compound and the holmium analogue is obvious. The features in the Dy system are more subtle, however they can be picked out. As the dc field increases more phase transitions are revealed. Using the same criteria as was used for the holmium, the phase diagram for hexagonal DyMnO$_3$ was created and is presented in Fig. C.7. The only previously published line [Ivanov et al. (2006)] is marked with open triangles. Dotted lines are through points that show a weak local maximum and may be associated with a gradual reorientation of the magnetic moments rather than an abrupt phase change. This argument was put forth to explain similar soft features seen in HoMnO$_3$ [Yen et al. (2007)].
Figure C.6 $\chi$ vs. $T$ for DyMnO$_3$ in five applied fields. The similarities between this compound and the holmium analogue are obvious.

Figure C.7 Phase diagram for hexagonal DyMnO$_3$. Filled black circles are TDR data and open red triangles are from Ivanov et al. (2006). Phases ITP and LTP are named following Nandi et al. (2008). Phases HT1 and INT are labeled as such under the assumption that they are similar to the other hexagonal rare earth manganites.
Interpretation of the Results

Interpretation of the TDR data in magnetically ordered samples is subtle. It is known that for local moment ferromagnets at the Curie temperature, zero field $\chi$ goes through a very narrow maximum provided the magnetic easy axis coincides with the rf coil axis. It is also known that magnetocrystalline anisotropy manifests at $T_C$ as a decrease in the growth of $\chi$ through $T_C$ when measured perpendicular to the easy axis as compared with parallel (see Ch. 2). Further, in antiferromagnetic metals [Prozorov et al. (2006)] no maximum in $\chi$ is seen at the Néel temperature, $T_N$, when the ordering axis is aligned with the rf coil axis. This can be understood once the amplitude of the rf field is considered. Such a small field is not able to overcome the AFM exchange interaction. If a given moment responds to the probe field, the magnetic coupling between it and its neighbors leads to a compensation of the induced moment. Therefore, there is no bulk change in the magnetization of the sample and the measured susceptibility shows no large response. This may be considered some zero field limit of the low temperature behavior of $\chi_{||}$. The situation in metals is further complicated by the fact that a magnetic field in the rf is screened from the bulk of the metal, thereby reducing the effective sample volume probed. Therefore, it is unclear what sort of response to expect from an antiferromagnetically ordered sample probed perpendicular to the ordering axis. Fortunately for the current work the rf screening is not a problem.

The magnetic symmetries of many of the phases of HoMnO$_3$ have been determined via second harmonic generation experiments [Fiebig et al. (2002b)]. For the hexagonal rare earth manganites the rare earth ions occupy two distinct lattice sites within the P6$_3$cm space group (2a and 4b) [Kamegashira et al. (2004)]. Each site may order differently from the other, depending on the temperature and field. Referring to Fig. C.3, phase HT1 has been identified as P6$_3$cm wherein the 2a Ho ions are free and the 4b ions exhibit AFM order along the $c$-axis. In HT2, all rare earth spins are in an AFM structure still aligned with the $c$ axis. The phase labeled INT has been identified as P6$_3$ where all the spins are antiferromagnetically aligned in the basal plane Yen et al. (2007). Phase LT2 has been identified as P6$_3$cm with all rare earth moments ordered parallel to the $c$ axis [Yen et al. (2007)]. The magnetic structure of phase
LT1 has not been identified.

With the previously published magnetic symmetries at hand, we can begin to understand the TDR data. Referring to Fig. C.2, between temperatures \( T_1 \) and \( T_2 \) there is an obvious enhancement of the \( c \) axis susceptibility. This is also the INT phase. On either side the moments order aligned parallel to the \( c \) axis. With the moments ordering in the basal plane, as occurs in INT, the rf field is inducing a coherent deflection, and hence a larger susceptibility results. At \( T_3 \) the system reenters the INT phase and at \( T_4 \) there is a return to \( c \) axis ordering in the phase HT1. Down to \( T_4 \) the transitions are superimposed on a Curie-like background. For temperatures less than \( T_4 \), however, there is a rapid decrease in \( \chi \). This would normally be associated with a fully ordered system. Based on the magnetic symmetry of the HT1 phase (which is presumed to exist in this region) there should be two free Ho moments. Normally these two spins would contribute significantly to \( \chi \). What can be inferred is that the impending full ordering of moments at \( T_5 \) leads to a slowing of the response of the free moments via exchange interactions.

Recent XRMS work on hexagonal DyMnO\(_3\) has allowed the phases labeled ITP and LTP in Fig. C.7 have been assigned the magnetic symmetries of P6\(_{3}\)cm and P6\(_{3}\)cm respectively [Nandi et al. (2008)]. The TDR data agrees with the XRMS data in the sense that both compounds exhibit similar features in \( \chi \) on crossing similar phase boundaries. The phase changes seen in the Dy compound are much more subtle than those from the Ho. This suggests that the moment size is not as critical in determining the interaction between the rare earth ion and the underlying lattice. Phase C has been identified in Er- and YbMnO\(_3\). In both of those compounds, as well as in the Ho version, this phase has the magnetic symmetry P6\(_{3}\)cm. In both the Er and Yb compounds the C phase is stable up to fields of approximately 0.5 kOe while in the Ho it exists all the way up to 10 kOe. If the Dy C phase has the same symmetry as the other members, then the low \( T \), low \( H \) behavior is closer to Ho than Er or Yb. The transitions from INT to LTP and A to B are associated with weak maxima in \( \chi \). These may be more evident in dielectric measurements. The well defined phases observed in DyMnO\(_3\) are qualitatively similar to the other \( RMnO_3 \) [Yen et al. (2007)].
Bibliography


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