Dysprosium and $\mathrm{GdCl_3}$ Curie Temperature Magnetic Susceptibility Measurements

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Magnetic phase transitions are not just indicators of the magnetic properties of a material, they also give insight into the exchange interactions that cause them. We measured the Curie temperature T_c which is the ferromagnetic-paramagnetic phase transition temperature for dysprosium (Dy) and gadolinium chloride ($\mathrm{GdCl_3}$). Using AC susceptometry between 2 K and 200 K we found T_c for $\mathrm{GdCl_3}$ to be either 2.22(5) K or 1.94(1) K (arrived at through independent analysis) which is in good agreement with the accepted value of 2.2 K[7]. We were unable to determine T_c in dysprosium due to a systemic thermometry error. Despite this, we qualitatively observed the Curie point and the Néel point in this material, and verified the Curie-Weiss Law in the paramagnetic region for dysprosium.

I. INTRODUCTION

A magnetic phenomenon of particular physical interest is that of ferromagnetization, or permanent existence of a bulk magnetic moment in a substance without the existence of an external magnetic field. Ferromagnetism can manifest only when the mutual alignment interactions of individual atoms dominate random thermal fluctuations. The force producing the tendency towards mutual alignment is not purely, or indeed predominantly, a consequent of the magnetic interactions of adjacent atomic dipole moments. Rather, the primary interaction force is mediated by an often little understood quantum mechanical effect known as the exchange force. Understanding the exchange force of a lattice can provide fundamental insights into the quantum nature of atoms, and thus measuring the exchange force for various atomic structures is an endeavor of great physical interest. The Curie point of a substance provides an effective probe of the exchange force.

Substances that display ferromagnetic behavior do so only below some critical temperature, T_c, known as the Curie temperature. Analysis of the Ising Model of magnetic atomic lattices demonstrates the appropriate definition of T_c is[4,6]:

$$T_c = \frac{2nJS(S+1)}{3k_b} \tag{1}$$

where n describes the number of adjacent connections for a given lattice site, S describes the atomic spin, k_b is Boltzmann's constant, and J is the strength of the exchange force. Above T_c, the random thermal fluctuations of the magnetic moments overwhelm the exchange force, preventing the formation of any bulk magnetic moment without an externally applied field. However, the atomic magnetic dipoles of a substance can still be aligned with the application of an external field, so substances that are ferromagnetic at temperatures below T_c are paramagnetic above it.

Perturbative analysis of the Ising model for $T > T_c$ reveals that the bulk magnetic susceptibility, χ, of N atoms of a paramagnetic substance with Curie temperature, T_c is given by the Curie-Weiss Law:

$$\chi = \frac{Ng^2\mu_b^2\mu_0 S(S+1)}{3k_b(T-T_c)} \equiv \alpha\frac{1}{T-T_c} \tag{2}$$

where g is the atomic factor relating magnetic moment to spin, μ_0 is the susceptibility of free space, μ_b is the Bohr magneton, N is the number of atoms in the substance, and α is a defined constant of proportionality to relate χ to the varying temperature. The perturbative nature of the calculation of equation 2 does not hold for $T \approx T_c$. However, the Curie-Weiss Law can still be used to measure T_c via linear interpolation of the T intercept of the measured relation between $\frac{1}{\chi}$ and T for $T > T_c$.

We report on the measurement of T_c for anhydrous gadolinium chloride ($\mathrm{GdCl_3}$) and dysprosium (Dy) via low temperature susceptometry.

II. EXPERIMENTAL METHODS

We measure the magnetic susceptibility of Dy and $\mathrm{GdCl_3}$ above T_c by warming a pair of inductor coils with a stored sample from low temperatures reached via submersion in, respectively, liquid nitrogen ($\mathrm{LN_2}$, $T = 77K$) and liquid helium (LHe, $T = 4.2K$). The coil pair consists of a primary drive coil over which the source voltage is applied and a secondary pick-up coil over which the signal voltage is measured. The secondary coil consists of a pair of identical, counter wound sub-coils, one of which contains the sample. The strength of the driving signal is determined by measuring the voltage drop over a known resistor in series with the drive coil. The output voltage from the secondary coil is read with a lock-in amplifier that is synchronized with the driving voltage. The temperature is determined from a thermometer thermally anchored to the sample. A heater is used to raise the sample temperature in steady increments. As discussed in the data analysis section, the measured values are used to determine the susceptibility as a function of T.

We provide a brief description of the various portions of our methods and procedure below, and refer the reader to the supplements for more details.

A. Outline of Apparatus

Our susceptometer consists of a pair of coils specially optimized to measure susceptibility of a small sample (refer to supplementary materials). Copper wire is wrapped around a hollow cylindrical shell to create the drive coil. A flaring cap on the top of the shell can be screwed to the cryostat probe. A series of grooves inside the shell allow the secondary coil chassis to be screwed into place inside the drive coil. A smaller cylindrical shell with two smooth winding regions separated by grooved region forms the chassis for the inner coil. A single length of copper wire is wound around both of the smooth regions with opposing orientations to produce the counter-wound pick-up coil[3,5]. The internal portion of one side of the pick-up chassis is threaded to allow for placement of a hollow screw that serves as the sample holder. A length of nichrome wire is wrapped around a sapphire rode to create a heater, and the rod is affixed in the hollow region of the screw. The sample is mounted on the end of the sample holder inserted into the pick-up coil and is thermally anchored to the thermometer via the sapphire rod. We use a resistive thermometer for the Dy measurement and silicone diode thermometer for the $GdCl_3$ measurement.

For more details, see supplement.

B. Outline of Electronics

Refer to Figure 1 for our circuit schematic and the supplements for greater detail. We attach the drive coil to a function generator in series with a known resistor to create the driving magnetic field. We measure the AC voltage drop across the known resistor with a Digital Multi-Meter (DMM). The output voltage of the secondary coil is directed to a lock-in amplifier synchronized with the function generator. A small voltage is applied across the heater with a Keithley voltage source. For the resistive thermometer, we use a DMM in 4 wire mode to both apply a known current and read the resulting voltage drop across the resistor. For the silicon diode thermometer, we supply a 10 μA current with a Lakeshore 201 Thermometer Controller and measure the voltage drop over the diode with a DMM.

C. Cooling Procedure

Once the sample holder was prepared as above, we affixed the sample holder to the end of a cryostat probe. For the Dy experiment, we filled a Dewar with LN_2, clamped the probe to a stable surface, and submerged the sample. For the $GdCl_3$ experiment, the need to use LHe necessitated a more sophisticated cooling procedure. We first placed the probe inside of the inner cavity of the cryostat and used a vacuum pump to reduce the internal pressure of the cavity to nearly 2 Torr. We filled the outer jacket of the cryostat with LN_2 to cool the internal cavity before proceeding to fill the cryostat with LHe.

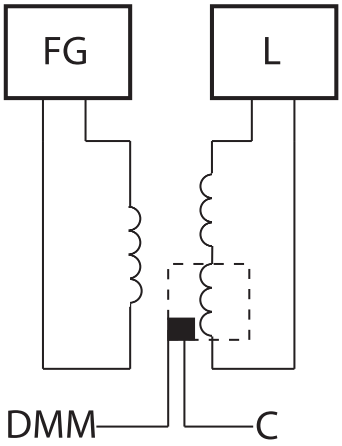

FIG. 1. Diagram of experimental apparatus: FG is an Agilent function generator, L is a lock-in amplifier, and C is the Lakeshore 201 controller. Our sample is mounted in the boxed region with an attached thermometer (black square).

D. Measurement Procedure

The following measurement procedure was automated with computer control. Please refer to the supplements for more information.

Once the sample was cooled, the heater was used to warm the sample and thermometer system in predefined increments. For the dysprosium measurements we used 1 K increments, while for the $GdCl_3$ sample, a finer resolution of 0.1 K was used. Once the desired temperature was reached, the temperature was held steady for the sample and thermometer to come to thermal equilibrium. At this point we measured the susceptibility (lock-in response), drive solenoid current, and the temperature again. This process was repeated over the design temperature range.

III. DATA ANALYSIS AND RESULTS

Here, we analyze our large body of collected data. We notice numerous magnetic structures in both Dy and $GdCl_3$ beyond the scope of the standard Curie-Weiss Law and discuss some possible sources of these structures associated with our AC susceptometry. We isolate a portion of our data that appears reasonably consistent with the Curie Weiss Law, and generate fits for (2). These fits yield a Curie Point of 1.8 K for $GdCl_3$. Due to systematic errors we are unable to adequately measure T_c in dysprosium, though we verify the Curie-Weiss law holds in the paramagnetic region. We also conduct a qualitative observation of the data to find distinctive phase transitions associated with transitions between different regimes of magnetic behavior. This qualitative examination yields values of the Curie Point of 2.2 K and 90 K for $GdCl_3$ and Dy. The data is collected with extremely high signal to noise, and we conlude our dominant source of error is the 4% systematic uncertainty associated with the lack of perfect cancellation in the counterwinding of the pick-up coil. Note that this systematic is only so large far away from the Curie temperature. In dysprosium, we identify and explain a systematic thermometry error preventing us from measuring the Curie temperature.

A. Standard Data Analysis Steps

Here, we provide a brief description of the analysis steps that were applied to both the $GdCl_3$ and Dy samples. A more detailed description is given in the supplements. Our measurement apparatus furnished us with four values: the measured magnitude of the voltage over the pick up coil, $|V|$, the current sent to the primary, I_P, the temperature of the measurement, T, and the phase of the signal with respect to the applied voltage, ϕ. The nature of our susceptometry apparatus informs us that $|V|$ should be proportional to χ and I_P. Thus, we know $\chi \propto |V|/I_P$. Further, as discussed in the conclusions and supplementary matieral, the AC nature of our experiment means the susceptibility must be modeled as consisting of a real component, χ', in phase with the input signal, and an imaginary component, χ'', out of phase with the input frequency. The DC susceptibility used in (2) corresponds most closely to real component of the complex AC susceptibility, however at the frequencies which we are using both the real and imaginary parts should obey the Curie-Weiss law with some critical exponent. Because there is also some calibration constant β in our susceptometer which we cannot account for, we define and measure

$$\gamma' = \beta\chi' = \frac{|V|\cos\phi}{I_P},$$

$$\gamma'' = \beta\chi'' = \frac{|V|\sin\phi}{I_P},$$

$$\gamma = \beta\chi.$$

Because we only intend to measure the transition temperature T_c, knowledge of γ suffices. Note that consequent of our analysis steps, γ has units of $\frac{\mathrm{V}}{\mathrm{A}}$. However, these units are of no physical significance.

B. Results for $GdCl_3$

To understand the possible impact a complex value of χ associated with AC susceptometry might have on our measurements, we cycled our measurements of the signal voltage of $GdCl_3$ through 4 different frequencies (as discussed in the methods section). We performed the above analysis for each of the frequency measurements. If the Curie-Weiss Law (2) were obeyed, we would expect a simple linear relation between γ^{-1} and T for $T > T_c$. However, Figure 2 is clearly not purely linear, suggesting the existence of additional magnetic phenomena.

One graphical structure of particular note is a distinct "kink" in the plots of γ^{-1} vs time at about 9 K. Consistently among all frequencies, the slope grows considerably steeper at this point, indicating some change in the susceptibility of the sample. A possible candidate for this kink is the existence of slight antiferromagnetism in the sample due to Gadolinium Oxide impurities[2]. Incidentally, the Curie-Weiss law intercept for the 2 kHz data above this kink is consistent with GdO_2 particles of a few μm in size. We concluded that attempting to fit across this obvious transition point with a single function would be ineffective, and so we opted to fit the data in the temperature range below 9 K with the following model derived from (2):

$$\gamma = \frac{A}{(T - T_c)^b} \tag{3}$$

with free paramaters A, b, and T_c: T_c giving the model's predicted Curie point and b generally taken to be 1 to match (2).

In the temperature range below 9K, we acquired the most data at 2 kHz, and we thus opted to fit only at that frequency. The measured values of γ are shown in Figure 2. We noted that the lowest few measurements vary significantly from the slope of the rest of the curve, likely indicating the transition betweeen parramagnetism and ferromagnetism (see below). We thus removed these data

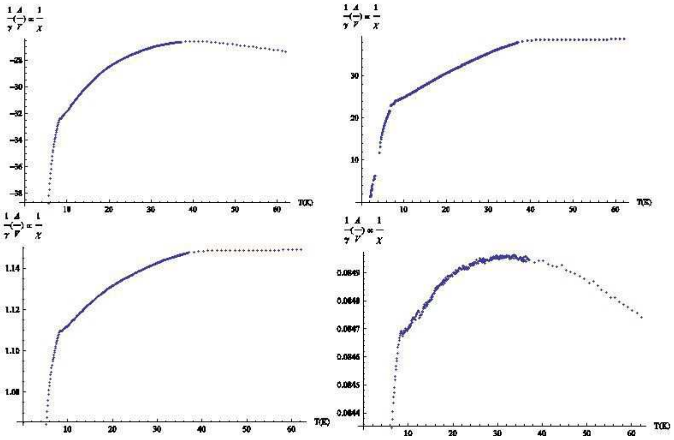

FIG. 2. Here we plot the measured values of $1/\gamma'$ vs T for all measured values at 1 kHz, 2 kHz, 4 kHz and 8 kHz (upper left, upper right, lower left, lower right respectively). All graphs clearly differ from the Curie Weiss Law. In particular, all show evidence of a distinct knee structure around T $9K$. Thus we opted to model only a portion of the data to measure T_c.

when performing our fit. Fitting this data according to (3) with $b = 1$ furnished predictions of $A = 0.186(5)\Omega K$ and $T_c = 1.94(1)K$ (see Figure 4). The errors were determined as discussed below. Allowing b to vary within a reasonable range did not change the best fit values significatnly. This portion of our data thus (according to the Curie Weiss Law) predicts a value of the Curie Point of $T_c = 1.94(1)$ K. The fit is again shown in Figure 4.

One might also measure the Curie Point from our data by visually determining the point at the smallest T value for which we observe a change in magnetic properties. In particular, looking at Figure 3 we notice that the magnitude of the slope γ vs T decreases suddenly near 2.22 K. One might reasonably associate this shift as a transition in the bulk magnetic properties of the sample. In particular, given the known low temperature ferromagnetic and parramagnetic properties of $GdCl_3$, we reasonably postulate that this observed transition indicates the sample's sudden shift from ferromagnetism to parramagnetism at T_c. Lack of granularity in the data and reasonable caution associated with measuring by inspection lead us to report an error of 0.05K for this claim.

Our measurements thus furnish two similar, but distinct measurements of T_c for $GdCl_3$. We predict a value of 1.94 K from a reasonably robust fit of the Curie-Wiess Law according to the model 3 and a value of 2.22 K determined by inspection of the transition behavior in χ associated with the shift in the sample's bulk magnetic properties. Ultimately, we feel the measurement yielded by inspection is the more likely candidate, as equation 2 is generally not believed to hold perfectly for values of T near the Curie Point.

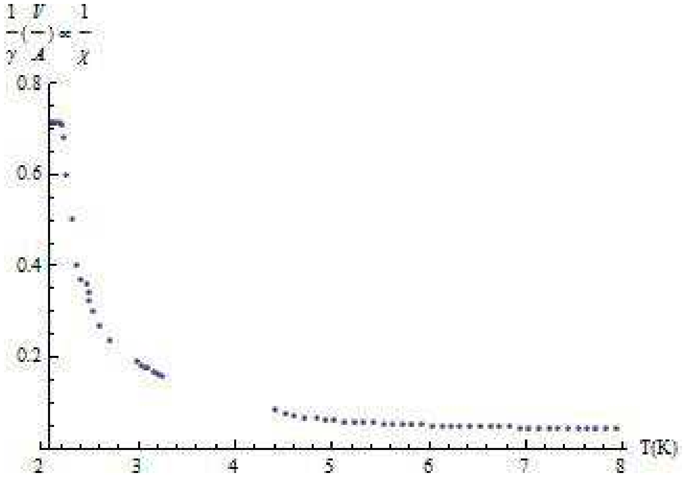

FIG. 3. Here we plot the measured values of γ' below 9K. Note that the data matches an inverse temperature graph reasonably well up until a small kink around 2.22 K. We take this transition as evidence of a shift in the sample from paramagnetism to ferromagnetism, and thus conclude T_c 2.22 K.

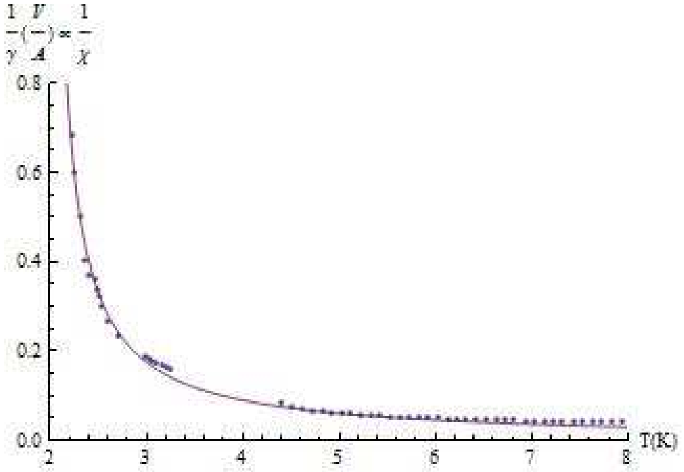

FIG. 4. Our measued values of γ' for $GdCl_3$ measured with an applied AC voltage of 2 kHz are shown in blue. The fit of the data according to equation 3 with $b = 1$ is shown in violet. The fit predicts a value of $T_c = 1.94(1)$ K.

C. Results for Dysprosium

For Dysprosium we took data from 90 K to 200 K in one degree intervals with a field strength of 100 μT at 2 kHz. The data has more or less the characteristics one would expect at a temperature just above a magnetic phase transition, as can be seen in Figure 5. We attempted to account for this peak in the susceptibility by considering sources of magnetic response other than the sample, but there were none strong enough to account for this phenomenon. After searching through data on the magnetic properties of dysprosium, we discovered however that between 85 K (the accepted value for $T_c^{[7]}$) and 179.8 K, dysprosium is actually antiferromagnetic with a Néel point (antiferromagnetic to paramagnetic phase transition T_N) at this hotter temperature.

If the observed peak in our susceptibility data really is the Néel point as we believe, then we are left with a systematic error in our thermometry of nearly 30 K. This is explained by the fact that for the dysprosium measurements we were forced to use a platinum resistance thermometer with an active sensing area much larger than was thermally anchored to the sample (see supplement). The implication is that despite the relatively poor thermal conductivity of nitrogen, it remains very likely that our thermometer was substantially colder than our sample, the mount for which was originally designed for use with a silicon diode sensor.

This sort of systematic is likely only to get worse with a larger temperature difference between the sample and nitrogen bath. With this in mind we fit the inverse susceptibility in at least a narrow trust region between 95 K and 105 K (see Figure 7), and above 153 K (see Figure 6); we expect the former will give an underestimate of T_c, but in better agreement with the published value. We do not fit $\Re(\gamma)$ in the latter region with an inverse linear

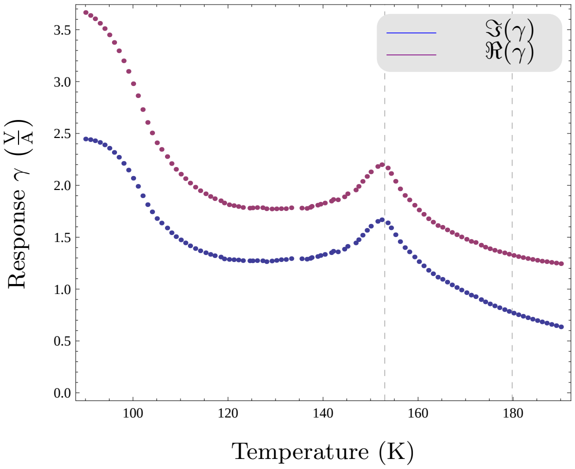

FIG. 5. Dysprosium susceptibility data showing an unexpected peak around 153 K (dashed line). The Néel point for dysprosium is 179.8 K. The real part of the response is plotted in purple and the imaginary part in blue.

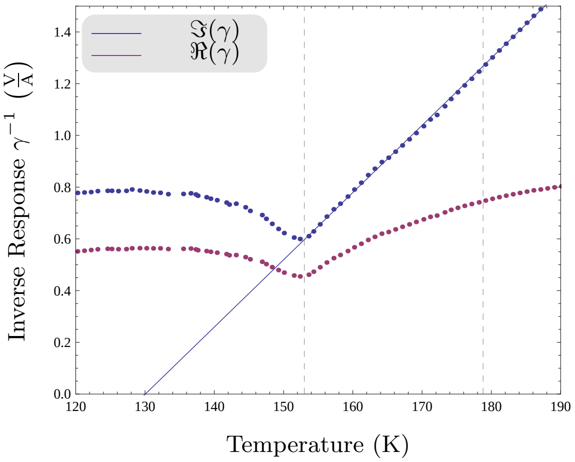

FIG. 6. Inverse dysprosium susceptibility with a linear fit on $\Im(\gamma)^{-1}$.

model, though in tests it appeared to follow the Curie-Weiss Law with critical exponent $\beta = 0.4(32)$. The data above 153 K shows a very linear relationship as predicted by the Curie-Weiss law, which adds further evidence to the case that our dysprosium was paramagnetic in this region and that we observed T_N at 153 K.

Having calibrated our coils at nitrogen temperature, our statistical errors are very small, with $T_c = 130.1(82)K$ as predicted from the data in the high temperature region in Figure 6, and $T_c = 77.(80)K$ from the low temperature region in Figure 7. Neither of these are in good agreement with the published values but both are consistent with the type of systematic error in thermometry described.

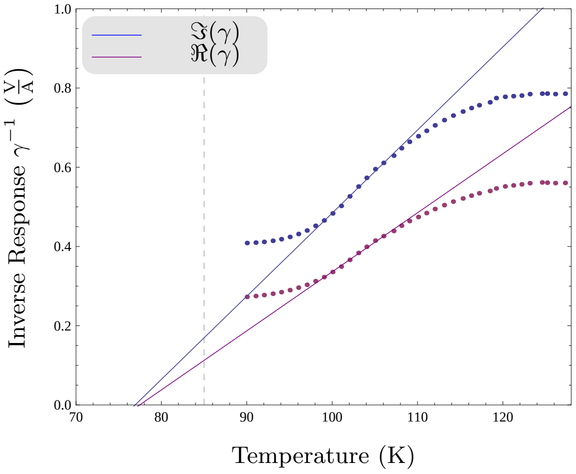

FIG. 7. Inverse dysprosium susceptibility

D. Determination of Dominant Error

Our signal was generally of order 100 μV, well above any statistical errors in our apparatus measurements. Thus, our predominant sources of error are systematic in nature. In particular, a slight asymmetry in the counterwiding of the pick-up coils constitutes the largest uncertainty in our measurements. Calibration tests run with an empty sample holder at both room and LN$_2$ temperatures indicated that their was a slight inductance associated with the empty pick-up coils. Our measurements indicate that, for 2000 kHz, this error would produce a maximal uncertainty in γ of 0.001 Ω, and we thus take that as our error in all reported values.

IV. CONCLUSION

We used AC susceptibility to measure the magnetic properties of dysprosium and gadolinium chloride at low temperatures. In particular, we successfully measured the Curie Point of GdCl$_3$ via two distinct techniques and observed expected qualitative behavior associated with the Curie and Neel Points of Dy. Despite systematic errors in thermometry, we were able to qualitatively characterize the magnetic phase transitions in dysprosium, observing a leveling at T_c and a peak at T_N, even though the temperatures we have associated which these vary significantly from the literature. We also confirmed that above the Néel point the Curie-Weiss Law holds as predicted. In future experiments, we would be sure to use the silicon diode thermometer for this measurement, in the hopes of eliminating the nearly 30 K systematic error at 153 K, as our apparatus was designed to maximize thermal conductivity with the sample for a thermometer of this much smaller size. For GdCl$_3$, our curves appear to visually indicate a Curie temperature of 2.22(5) K, with error due to granulation of the data. Fitting our data according to (3) with $b = 1$ gave a predicted Curie temperature of 1.94(1) K, compared to the reported literature value of 2.2 K. Further exploration of the potential impurities in our sample would allow us to explain the additional magnetic phenomenon of the knee at 9 K for all measured frequencies.

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