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SPIN GLASS TRANSITIONS IN GEOMETRICALLY FRUSTRATED MAGNETS

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Abstract

Spin glasses are magnetic systems exhibiting both quenched disorder and frustration, and have often been cited as examples of 'complex systems.' At the spin glass "freezing temperature" the spins stop fluctuating but do not exhibit long range orientational order. Geometrically frustrated magnets often exhibit spin glass behavior. In this paper spin glass physics is briefly discussed. We then discuss geometrically frustrated magnetism. This is followed by a discussion of experimental data taken in the lab on the magnetic freezing temperature of two different frustrated materials in various external magnetic fields. Two different known geometrically frustrated spin glass materials were cooled to helium temperatures. Magnetic moment data were collected at various different temperatures through two cycles, one prepared by cooling in zero external magnetic fields (zero field cooled), and the other by cooling in fields (field cooled). The freezing transition is compared to the expected magnetic field using two models and we find our data to be in agreement with the de Almeida-Thouless prediction for Ising spins, surprising considering that Cr^{3+} carries a Heisenberg-like spin.

Introduction

A broad overview of spin glass physics and geometrically frustrated systems will be presented, as well as the analysis of freezing properties of two materials, ZnCr_2O_4 and $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$. First, we must give an introduction to spin glass physics.

What is a spin glass?

Spin glasses are compounds with localized magnetic moments, whose interactions are characterized by *quenched disorder*, (disordered state which is not in thermodynamic equilibrium, but nevertheless static in the temperature range interest) where a pair of spins have an equal probability of being aligned, or anti-aligned (fig. 1). Such a situation is referred to as frustration. Another class of materials, referred to as *geometrically frustrated*, is where atoms are interacting antiferromagnetically and sit on lattice sites based on triangles.

Some of the first types of material for spin glasses were dilute magnetic alloys, which have a small amount of magnetic impurity doped into the lattice of a nonmagnetic metal, for example FeAu where low concentrations of iron in the gold lead to spin glass physics. Note that insulators also show spin glass behavior, but under different circumstances.

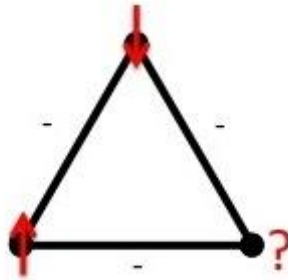


Figure 1. Triangular lattice showing a frustrated spin.

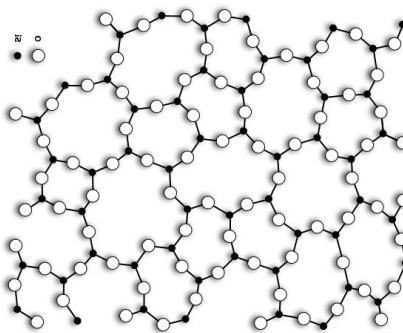


Figure 2. An example of randomly distributed, non-trivial lattice.

The physics for dilute metal alloys comes from the conduction electron-mediated RKKY (Ruderman-Kittel-Kasuya-Yoshida) interactions between the localized moments. Early experiments by Cannella and Mydosh [1] showed that a phase transition took place in FeAu alloys where the low field ac magnetic susceptibility χ_{ac} , exhibited a cusp at a frequency dependent temperature T_f . Similar behavior has been seen in other spin glasses, for example insulating systems like $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ with x ranging from 0.13 – 0.50 [10] have a dipolar interaction between spins that causes this cusp in χ with the characteristic frequency dependence of spin glasses.*¹

Several different experiments have shown that at or below a critical freezing temperature, the spins are frozen, for any reasonable observational time scale, in random orientations. Another important feature is that spins respond to an applied field with a distribution of relaxation times

Spin glass theory

The modern theory of spin glasses began with works by Edwards and Anderson (EA), who proposed that the essential physics would be found in the competition between quenched up and down spin interactions at long range. The Hamiltonian used in the EA model is

$$H = - \sum_{\langle ij \rangle} J_{ij} S_i S_j, \quad (1)$$

where S_i refers to the Pauli spin matrix for the spin half particle at lattice point i . A negative value of J_{ij} denotes an antiferromagnetic interaction between spins at points i and j . The sum runs over all nearest neighbor positions on a lattice and J_{ij} is a random variable.

Equation 1 can be used to solve for the critical temperature or freezing temperature of a particular spin glass material as well as prove its “glassy structure” (fig. 2).

Frustration

The Hamiltonian (1) exhibits *frustration*: no spin configuration can simultaneously satisfy all couplings (fig.1) for random interactions. If a closed circuit O in the edge lattice satisfies the property

$$\prod_{\langle x,y \rangle \in O} J_{xy} < 0, \quad (2)$$

then the spins along the lattice can't all be simultaneously satisfied [1]. Anderson suggested a different formulation, namely that frustration manifests itself as free energy fluctuations scaling as the square root of the surface area of a typical sample. Either way, the spin glass is characterized by both quenched disorder and frustration. Their joint presence indicates the possibility that spin glasses might possess multiple pure thermodynamic states unrelated by any simple symmetry transformation.

Statistical Mechanics of Disordered Systems

Homogenous systems, such as crystals, uniform ferromagnets and superfluids display spatial symmetries that greatly simplify their physical and mathematical analyses. In the absence of such symmetries, vast complications in the understanding tend to arise in disordered systems like spin glasses. This may lead to new types of broken symmetries, a breakdown of the thermodynamic limit for certain quantities, and the need to create new thermodynamic tools. True, statistical mechanics should not, and would not be rewritten in order to understand such disordered systems, as has been suggested at times, but it is at least necessary to carefully rethink some deeply held assumptions.

¹ Though this cusp in χ is in fact necessary, it is not sufficient evidence to signify spin glass behavior.

Mean Field Theory

Shortly after the emergence of the Edwards Anderson model, an infinite ranged version was proposed by Sherrington and Kirkpatrick. For a system of N Ising spins and in zero field, their Hamiltonian is

$$\mathcal{H}_{J,N} = -\frac{1}{\sqrt{N}} \sum_{1 \leq i \leq j \leq N} J_{ij} \sigma_i \sigma_j, \quad (3)$$

where the independent, identically distributed couplings J_{ij} are chosen from a Gaussian distribution with zero mean and variance one. The $1/\sqrt{N}$ scaling ensures a plausible thermodynamic limit for free energy per spin and other thermodynamic quantities. Given the infinite ranged aspect of this model, it was widely accepted as it was exactly solvable. According to the SK solution, the spin glass susceptibility is really negative. This is not only in contradiction with experiment, but also with the correlation-function susceptibility which is positive definite [9]. The SK model proposed incorrectly, the behavior at the critical temperatures as well as negative values of entropy at very low temperatures. A mean field theory was proposed two years later by Thouless, Anderson and Palmer [6], whose approach determined that there may be many low temperature solutions, possibly corresponding to different spin glass ‘phases’.

Applications to Other Areas

Applications of spin glass physics abound in areas as diverse as computer science, neural networks, prebiotic evolution, protein conformational dynamics, protein folding and a variety of others. We will not have time to discuss these applications here, but extensive treatments can be found in [3-5].

Geometrically Frustrated Magnets

Long range order in spin glasses is prevented by the frustration arising from disorder. In the class of geometrically frustrated magnets (GFM), long range order is suppressed by symmetry reasons alone. GFMs are systems where the antiferromagnetically-interacting spins lie on the triangle-based lattices. Since the work of Wannier [9] it has been known that, in idealized models of triangle-based systems, long range order occurs at temperatures much lower than expected from mean field theory, and in some cases, leads to entropy at zero temperature, a seeming violation of the 3rd law of thermodynamics. These ideas were shown to have many examples in real compounds by Ramirez [8], who in 1994 catalogued the known GFMs and provided a simple way to identify them experimentally. It came as an early surprise that, even in materials with very low amounts of quenched disorder, some GFMs exhibit spin glass behavior. Compared to the conventional spin glass materials, GFMs represent a relatively unexplored materials class for the study of spin glass physics.

What are we doing?

Given that typical spin glasses display geometrical frustration as well as quenched disorder, in our lab we are experimenting with certain compounds which display a low degree of disorder as well as very high geometrical frustration in hopes that extraordinary physical phenomena will be observed due to the uniqueness of material we are observing. These are the objectives for the whole lab, however for this thesis, the research done was focused on studying $\text{Zn}(\text{Cr,Ga})_2\text{O}_4$ and $\text{Sr}(\text{Cr,Ga})_9\text{Ga}_3\text{O}_{19}$ with a 5% defect concentration of Ga substituted for Cr. In both of these compounds the Ga is non-magnetic, the Cr is magnetic, having a valence of 3⁺, and the associated spin value of 3/2. It should also be noted that the spin 3/2 on Cr³⁺ is a Heisenberg spin. We will also verify two equations from Binder and Young [2] for the temperature field phase diagram

$$H_{Ising}(T) \propto \left(1 - T/T_f\right)^{3/2} \quad (4)$$

and

$$H_{XY}(T) \propto \left(1 - T/T_f\right)^{1/2} \quad (5)$$

for the two materials, where H is the external magnetic field strength, T_f is the corresponding freezing temperature and T is a temperature just higher than the highest freezing temperature. Eqn. (4) corresponds to the “AT line” (de Almeida and Thouless, 1978), which occurs in Ising spin glasses with infinite-range random interactions, while eqn. (5) corresponds to the “GT line” (Gabay and Toulouse, 1981), which predicts the freezing in of the transverse components of spins [2]. Equations 4 and 5 serve merely as a theoretical guide to SG behavior. The GT line rarely occurs.

Data, Analysis and Methods

In order to collect data from our samples, we followed the following procedure: first the sample was placed within a gelatin capsule, then the capsule was inserted into an ordinary soda straw with a nylon string. The straw was then attached to the metal rod which moved vertically via a stepping motor. The magnetometer is a Quantum Design Magnetic Property Measurement System, which provides highly accurate and precise magnetization data by the integration of a Superconducting Quantum Interference Device (SQUID) with a set of coils designed to minimize the influence of external fields. The sample is uniformly drawn through the SQUID coils by the MPMS software and the temperature, magnetic field and magnetization are recorded. A simple temperature-field sequence controlled the data acquisition. The typical data acquisition sequence consisted of two parts, zero field cooled (ZFC) and field cooled (FC). During the ZFC portion, the sample was cooled to the base temperature (2K) in zero magnetic field. The field was then applied to the sample, and data were acquired on increasing temperature. For the FC measurements, the temperature was brought to the upper limit of the ZFC sequence, a field was applied and data were taken as the temperature was decreased along the same intervals as the ZFC scan. The ZFC/FC sequence was repeated for several different values of the external magnetic field. It should be noted here that after each cooling portion, the temperature was brought back up to the initial starting temperature and stabilized before again collecting data. This process was repeated with a similar sequence for the second sample.

The majority of the research for this thesis was interpreting the data from the computer, which was able to make such precise measurements.

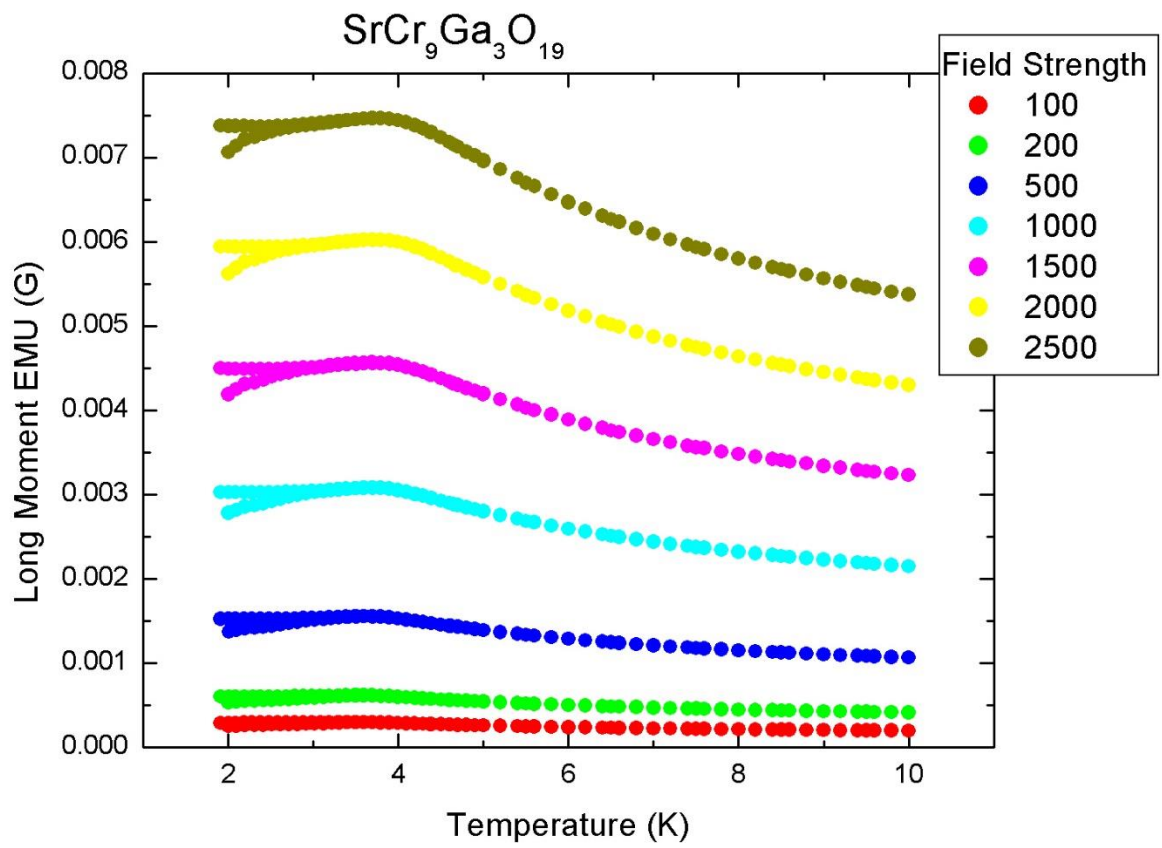


Figure 3. The six runs through the helium bath for $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$ are shown. The bifurcation exhibits the zfc line (lower curve) and the fc line (upper curve). The vertical axis measures longitudinal moment.

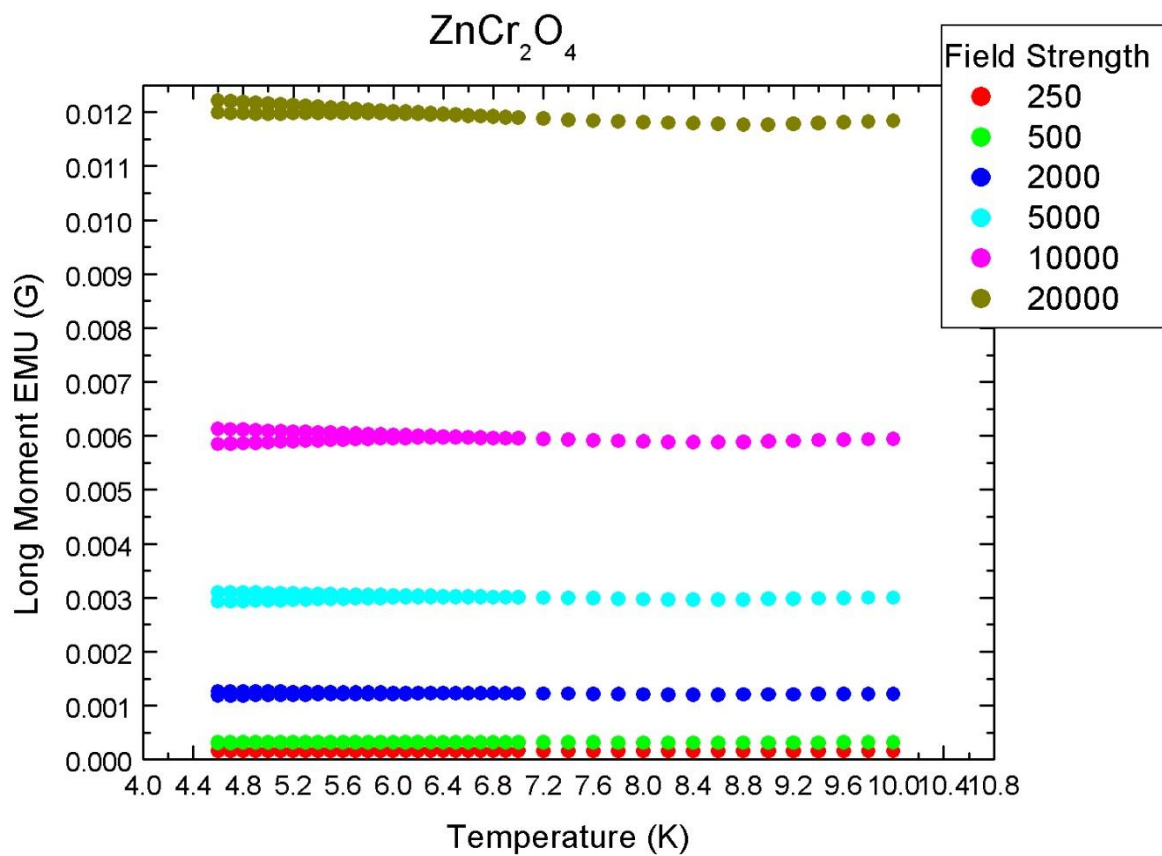


Figure 4. The six runs through the helium bath for ZnCr_2O_4 are shown. The bifurcation exhibits the zfc line (lower curve) and the fc line (upper curve). The vertical axis measures longitudinal moment.

Figures 3 and 4 show all the runs through the helium bath with which data was collected. A more effective plot at this time will be a single run (Fig. 5).

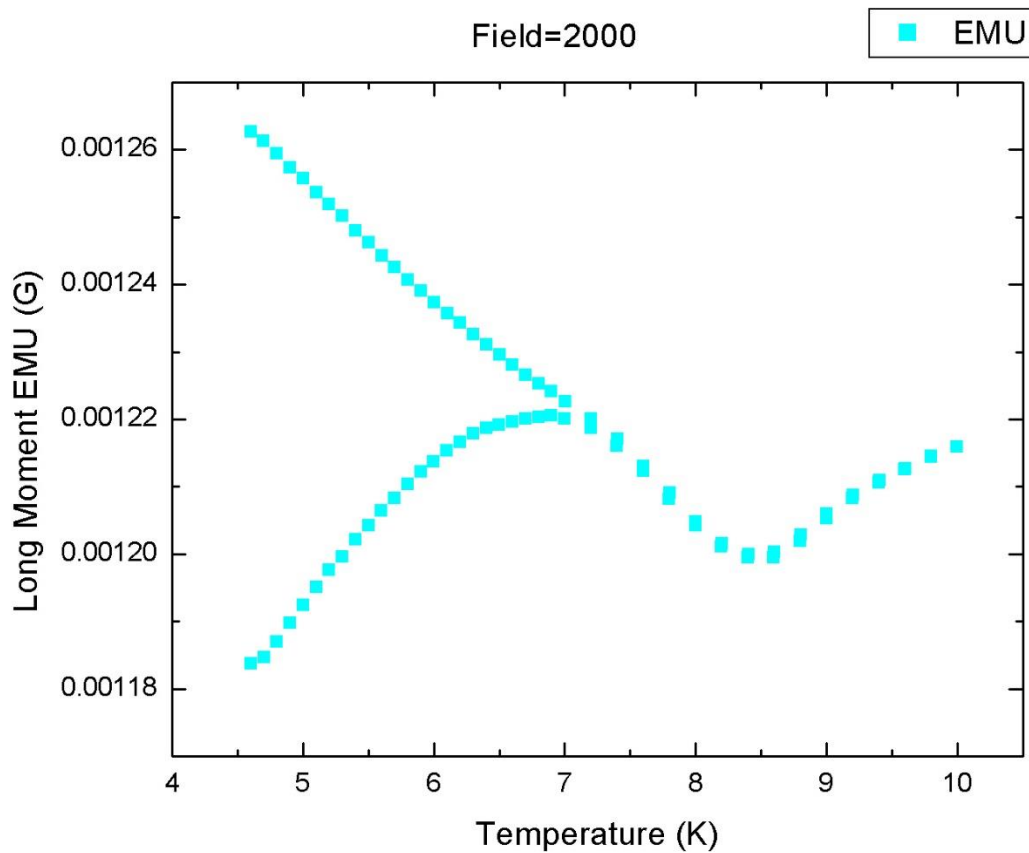


Figure 5. ZnCr_2O_4 magnetic moment vs. temp. External magnetic field= 2000G

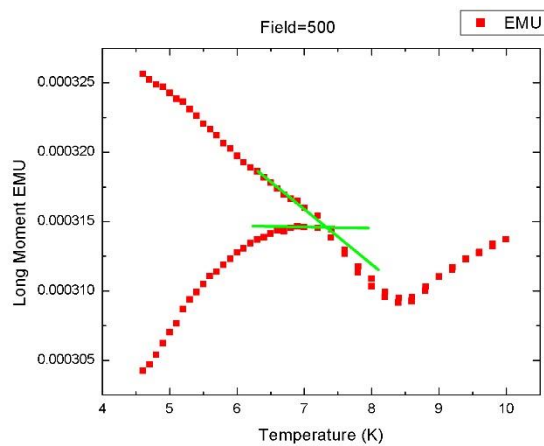


Figure 6. A plot of the straight line construction method used for finding T_f .

Plots for each run for both samples were obtained and the freezing temperature of the samples were determined by zooming in on the diverging curves. We used a straight line construction (fig.6) to determine the freezing temperature, the point at which the two straight lines cross. This point is the experimental freezing temperature, T_f of the sample at the given field. Once the freezing temperatures were determined (Tab. 1), the data interpreting and analyzation could commence.

SrCr₉Ga₃O₁₉		ZnCr₂O₄	
Field (G)	Temp (K)	Field (G)	Temp (K)
1 x10 ²	3.47	2.5x10 ²	7.813
2 x10 ²	3.438	5x10 ²	7.574
5 x10 ²	3.385	2x10 ³	7.353
1 x10 ³	3.089	5x10 ³	7.29
1.5 x10 ³	3.01	1x10 ⁴	7.156
2 x10 ³	2.84	2x10 ⁴	6.889
2.5 x10 ³	2.829		

Table 1. Magnetic field (G) and corresponding freezing temperature (K) for both samples.

A compilation of all of the data and plots will be appended to this document, however in the main body we will only pertain to a pragmatic, discrete set.

Having measured multiple freezing temperatures for each sample, next was to manipulate the data to attempt verifications of eqns. 4 and 5. First was to plot H vs. T data for each sample, where H is the applied field and T is the freezing temperature. Next was to make a new spreadsheet with the x column running from 0 to 1 in 0.1 increments. This x column was multiplied by the T_f value at $H = 0$. Finally, a new y column was set using both eqns. 4 and 5. This was done for both samples. Note that for the particular samples used, it turned out that eqn. 5 was not applicable. Linear regression was not used but rather a visual fit by varying the theoretical parameter was utilized. This method was sufficiently accurate to test the hypothesis of AT vs GT lines.

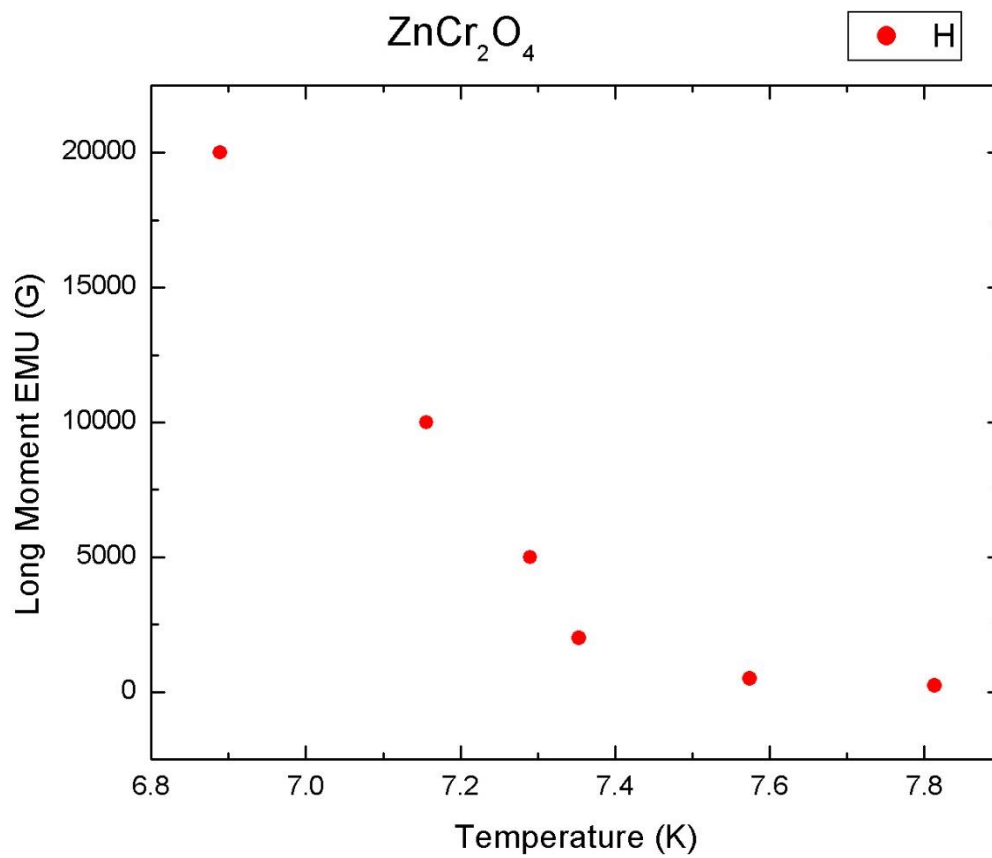


Figure 7. The applied external magnetic field vs. measured freezing temperature for ZnCr_2O_4 .

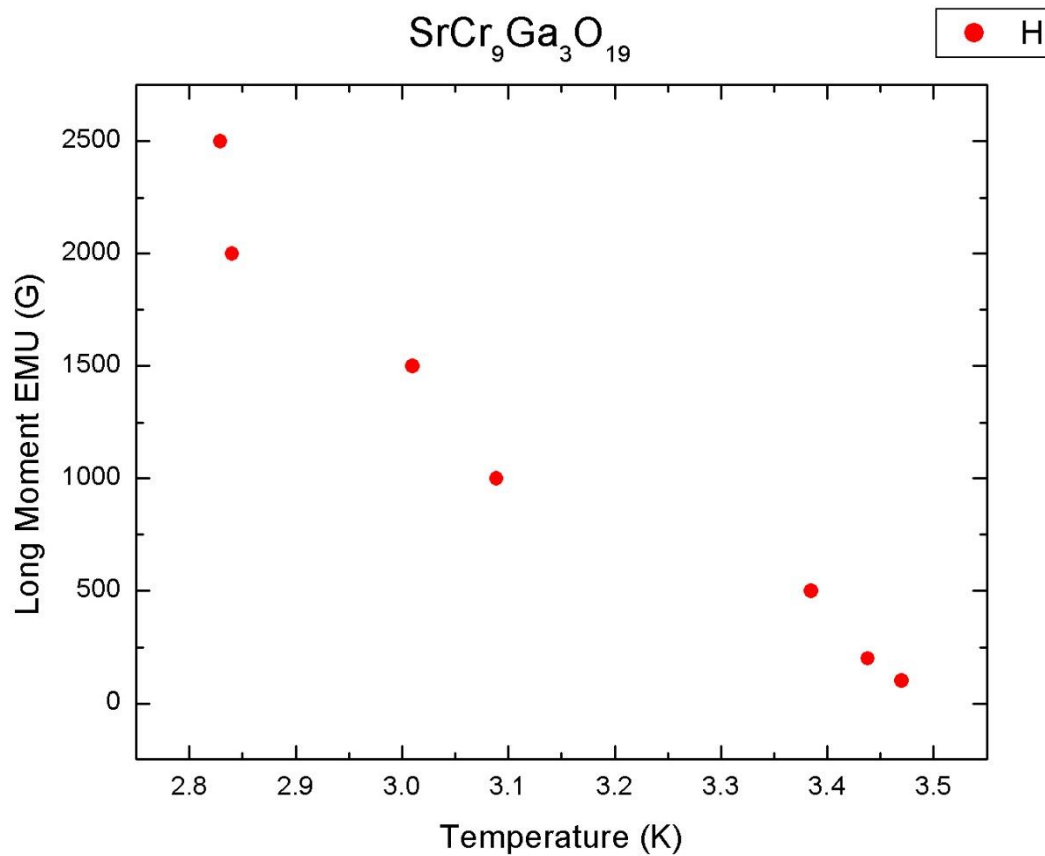


Figure 8. The applied external magnetic field vs. measured freezing temperature for $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$.

$\text{SrCr}_9\text{Ga}_3\text{O}_{19}$		ZnCr_2O_4	
Field	Temp	Field	Temp
1.9×10^4	0.35	2.9×10^5	0.785
1.6×10^4	0.7	2.4×10^5	1.57
1.3×10^4	1.05	1.9×10^5	2.355
1×10^4	1.4	1.5×10^5	3.14
8.1×10^3	1.75	1.2×10^5	3.925
5.8×10^3	2.1	8.6×10^4	4.71
3.7×10^3	2.45	5.5×10^4	5.495
2×10^3	2.8	3×10^4	6.28
7.2×10^2	3.15	1×10^4	7.065
0	3.5	0	7.85

Table 2. An adjusted version of the applied magnetic field (G) to make up for the multiplicative constant in eqn. 4 and corresponding freezing temperatures (K) notched by 0.1 increments for both samples.

The equations used to produce the *Field* columns in table 2 are

$$H_{ZC} = A \left(1 - \text{col}(\text{temp})/7.85\right)^{3/2},$$

for ZnCr_2O_4 and

$$H_{SGO} = B \left(1 - \text{col}(\text{temp})/3.5\right)^{3/2},$$

for $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$. Where A and B are 3.4×10^5 and 2.3×10^4 respectively, which are the proportionality constants required to bring the experimental data vs. AT/GT line theory to a measurable proportion, with units of Gauss. Next was to plot tables 1 and 2 in concurrence to verify a good fit.

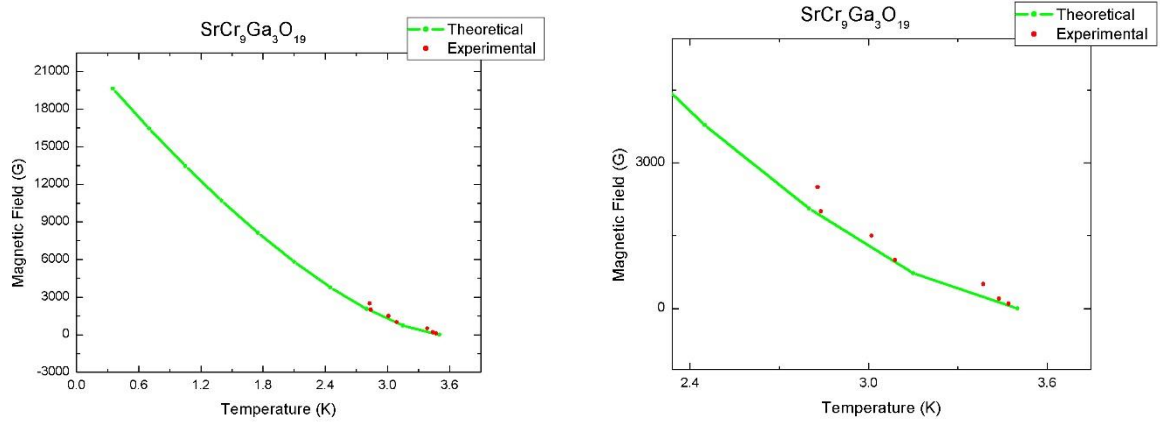


Figure 9. Experimental field vs temp (red) layered with theoretical field vs. temp (green) for $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$ using eqn. 4 and the magnified portion.

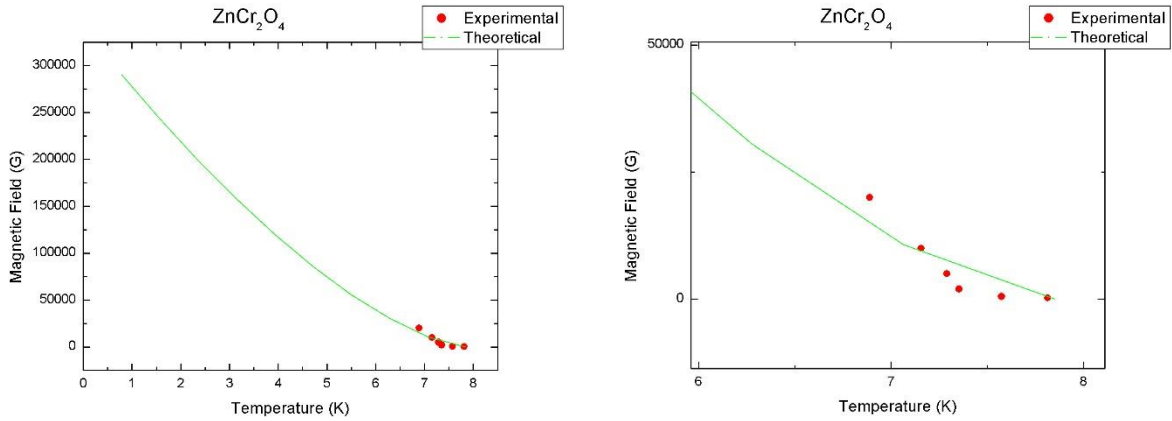


Figure 10. Experimental field vs temp (red) layered with theoretical field vs. temp (green) for ZnCr_2O_4 using eqn.4 and the magnified version.

Now to demonstrate how eqn. 5 did not make a suitable fit for our experimental data. First, table 3 below will give the adjusted field and temperature data just as before.

SrCr ₉ Ga ₃ O ₁₉		ZnCr ₂ O ₄	
Field	Temp	Field	Temp
2.1 x10 ⁴	0.35	2.8 x10 ⁴	0.785
2 x10 ⁴	0.7	2.6 x10 ⁴	1.57
1.9 x10 ⁴	1.05	2.5 x10 ⁴	2.355
1.7 x10 ⁴	1.4	2.3 x10 ⁴	3.14
1.6 x10 ⁴	1.75	2.1 x10 ⁴	3.925
1.4 x10 ⁴	2.1	1.8 x10 ⁴	4.71
1.2 x10 ⁴	2.45	1.6 x10 ⁴	5.495
1 x10 ⁴	2.8	1.3 x10 ⁴	6.28
7.2 x10 ³	3.15	9.4 x10 ³	7.065
0	3.5	0	7.85

Table 3. An adjusted version of the applied magnetic field (G) to make up for the multiplicative constant in eqn. 5 and corresponding freezing temperatures (K) notched by 0.1 increments for both samples.

The equations used to produce the *Field* columns in table 3 are

$$H_{ZC} = C \left(1 - \text{col}(\text{temp})/7.85\right)^{1/2},$$

for ZnCr₂O₄ and

$$H_{SGO} = D \left(1 - \text{col}(\text{temp})/3.5\right)^{1/2},$$

for SrCr₉Ga₃O₁₉. Where *C* and *D* are 3x10⁴ and 2.3x10⁴ respectively, which are the proportionality constants required to bring the experimental data vs. AT/GT line theory to a measurable proportion, with units of Gauss. It can be seen from plots of these theoretical values layered with the experimental data that eqn. 5 does not make a good fit for SrCr₉Ga₃O₁₉ or ZnCr₂O₄.

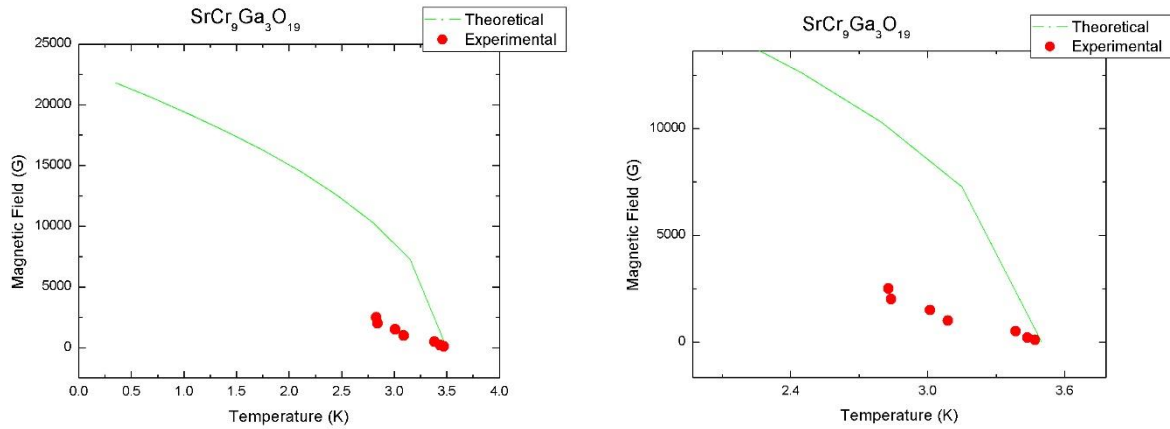


Figure 11. Experimental field vs temp (red) layered with theoretical field vs. temp (green) for SrCr₉Ga₃O₁₉ using eqn. 5 and the magnified version.

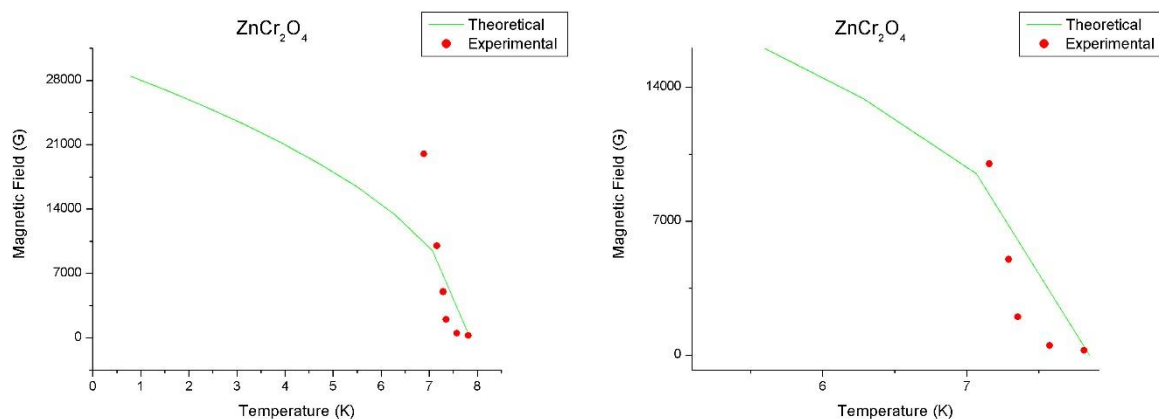


Figure 12. Experimental field vs temp (red) layered with theoretical field vs. temp (green) for ZnCr_2O_4 using eqn.5 and the magnified version.

Note that a collection of all of the raw data is available upon request.

Conclusion

The main focus of this research project was to test the hypothesis of whether the field dependence of the freezing transition temperature is better described by an Ising theory (AT line) or by a Heisenberg theory (GT line). As a consequence of plotting tables 1 and 2, it was possible to decipher the data and make an estimate as to whether the data formulated a proper verification of eqns. 4 and 5. As stated previously, eqn. 5 did not make a good fit to experimental data however was shown in figs. 10 & 11 for quantitative purposes. On the other hand, eqn. 4 conformed quite well to the experimental data, henceforth we propose here that eqn. 4 was verified through experimental means and that both ZnCr_2O_4 and $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$ spin glasses have Ising spins following the “AT line.” This conclusion quite surprising as we were predicting Heisenberg-like spins; in order to come closer to theoretical predictions, more research is required. Some further experimentation could involve lower temperatures, different materials, different defect concentrations of materials or higher fields.

Our exploration of spin glass materials and their low temperature magnetic phase transition is still in its premature state; there is still much to learn and many more steps to take. This experiment was just the tip of the iceberg for spin glass phenomena in geometrically frustrated magnets. Learning that these materials are indeed the type that exhibit known spin glass properties allows us to take further action into discovering new properties in the field. There is still much to learn in mean field theory and the physics of spin glasses, and like the development of any field, this one has gone and will go through many revisions before one idea is uniformly accepted.

Having verified eq. 4 was quite the pleasant outcome at the end of the experiment. Had there been more time, it would be beneficial as well as fun and meaningful to continue the process with different samples in order to verify eqn. 5. In any case, any future work done with low temperature condensed matter physics.

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