

# Coexistence of Ferromagnetic and Glassy States in Mechanically Milled $\text{GdAl}_2$

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Measurements of DC susceptibility, AC susceptibility, and AC susceptibility with an applied DC bias field were performed on mechanically milled  $\text{GdAl}_2$ . A paramagnetic phase exists above a temperature  $T \approx 140$  K. However, there are significant deviations from the Curie-Weiss Law in this temperature regime, suggesting multiple magnetic components. Fits to the high temperature data show that two Curie-Weiss terms represent the data quite well. Below 140 K one of these magnetic components becomes ferromagnetic as indicated by a shoulder in the AC susceptibility and DC susceptibility data. This ferromagnetic component is suppressed by the application of sufficiently strong DC bias field. Accompanying this shoulder is a peak at lower temperatures ( $T < 50$  K), which suggests the existence of another component that is magnetically glassy in nature. The two-component behavior of mechanically milled  $\text{GdAl}_2$  can be explained in terms of the nanostructure of the material, which consists of nanometer-sized grains and a disordered interphase.

## I. INTRODUCTION

The existence of a magnetically glassy state in mechanically milled  $\text{GdAl}_2$  has been well established in recent papers [1]. However, the true nature of this glassy state has not yet been determined.

Mechanical milling of bulk  $\text{GdAl}_2$  provides the necessary components for a glassy state. The two necessary ingredients for a spin-glass are randomness and frustration [2]. Mechanical milling introduces randomness in the  $\text{GdAl}_2$  crystal lattice by means of quadruple defect disorder [1]. Aluminum (Al) can replace Gadolinium (Gd) on the Gd sub-lattice, but Gd cannot replace

Al because of the large size difference in the two atoms. As a result, four defects are essentially created in a single Al-Gd substitution and a disordered system is created.

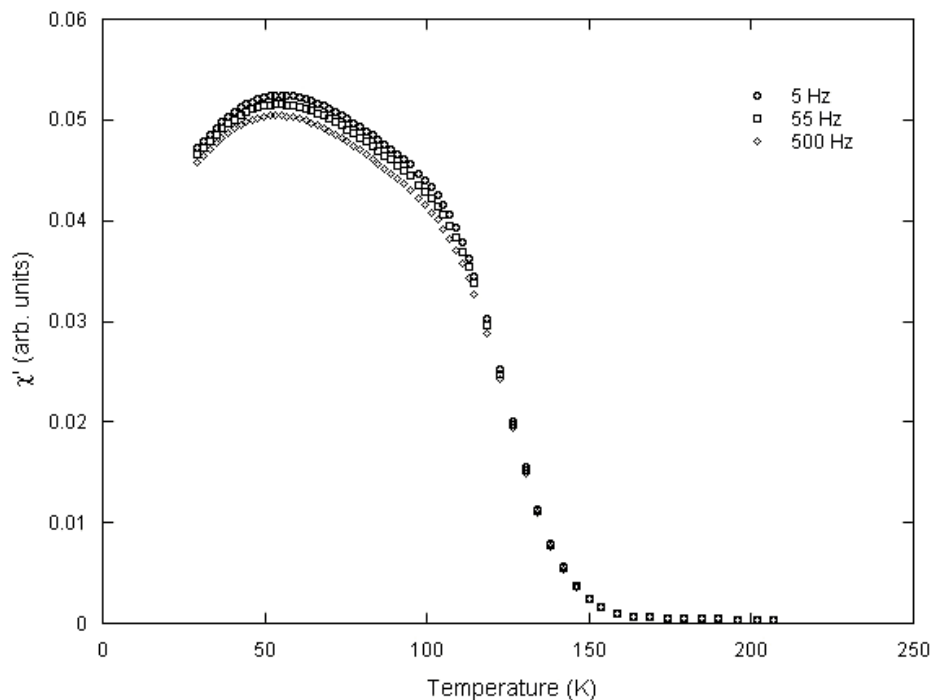
Frustration results from the inability of a system to simultaneously minimize the exchange energy of each of its interactions. Instead, the system relaxes to a state in which all interactions are equally unsatisfied [3]. In mechanically milled  $\text{GdAl}_2$ , this structural frustration is due to the disorder induced by mechanical attrition and RKKY exchange interactions. The itinerant electrons in  $\text{GdAl}_2$  act as intermediaries in RKKY

interactions, causing an exchange coefficient,  $J$ , that fluctuates from positive to negative as a function of distance between the two magnetic (Gd) atoms. Thus, the orientation of the spins that minimizes the exchange energy depends on the distance between Gd atoms. Considering the simplest Ising model, the spins could be parallel or anti-parallel when the energy is minimized. When considering more than two interacting atoms, it becomes clear that not all of the spins will necessarily be able to align themselves in their preferred orientation. As a result, this disordered system becomes frustrated.

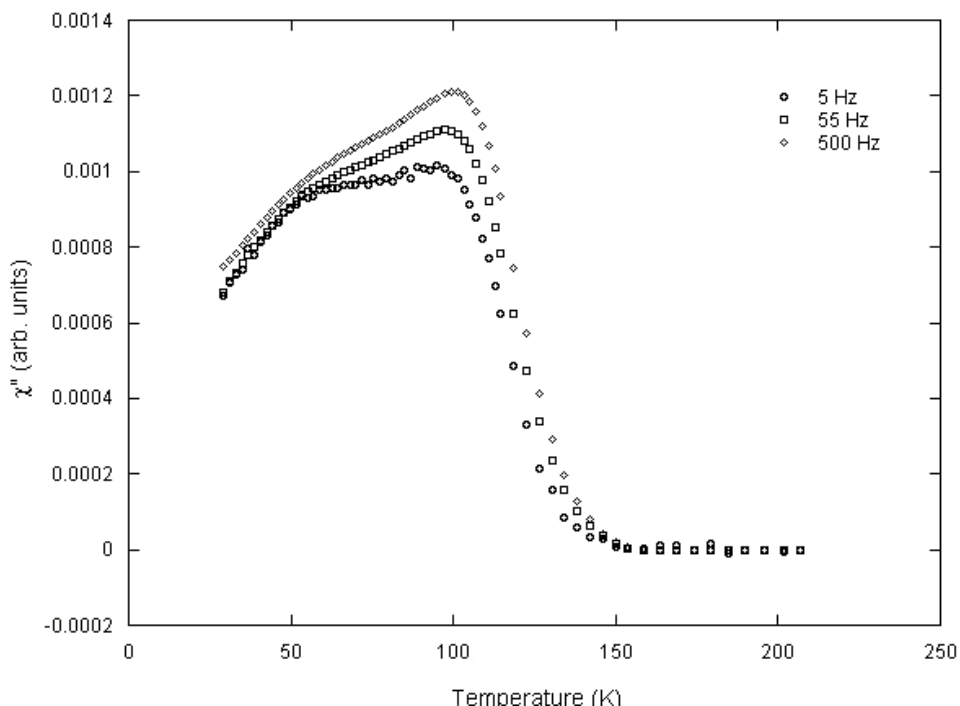
In addition to RKKY, Gd ions in mechanically milled  $\text{GdAl}_2$  may also interact via superexchange, another exchange interaction. In superexchange, three atoms must have overlapping electron wavefunctions. P electrons in the nonmagnetic atom (Al) act as the intermediary, due to its overlapping outermost electron wavefunction with the wavefunctions of two magnetic atoms (Gd). Because of the Pauli Principle, the spin of the outermost electron in the nonmagnetic ligand opposes the net spin of the electrons in the magnetic atom [4]. This can lead to a ferromagnetic or

antiferromagnetic alignment. These exchange interactions can lead to vastly different behavior depending on the extent of disorder induced by milling in the  $\text{GdAl}_2$  sample.

It is well known that for bulk  $\text{GdAl}_2$ , there exists a ferromagnetic-paramagnetic (FM-PM) transition at  $T_c \approx 175$  K. The paramagnetic region can be well fit using a simple Curie-Weiss equation,  $\chi = C/(T - \theta)$ , where  $\chi$  is susceptibility,  $C$  is the Curie constant,  $T$  is the temperature, and  $\theta$  is the Curie-Weiss temperature, which is close to  $T_c$ . The transition between FM and PM states of bulk  $\text{GdAl}_2$  can be understood in terms of a competition between exchange and thermal energies. In the non-cooperative paramagnetic region, the thermal energy dominates and the magnetic moments of atoms flip randomly, leading to a positive, temperature-dependent susceptibility, as shown by the Curie-Weiss Law. At  $T_c$ , the thermal energy equals the exchange energy of the system and the system becomes ordered. In the ferromagnetic region, the exchange energy dominates and the Gd moments align parallel within domains.



**Figure 1.** AC Susceptibility of 350-hour sample  $\text{GdAl}_2$  at 1 Oe [Oersted], showing the in-phase component of susceptibility as a function of temperature,  $\chi'$  vs.  $T$ .



**Figure 2.** AC Susceptibility of 350-hour sample  $GdAl_2$  at 1 Oe., showing the out-of-phase component of magnetic susceptibility as a function of temperature,  $\chi''$  vs. T.

It is also well known that in amorphous  $GdAl_2$  there exists a spin glass phase transition at approximately 16 K [5]. However, in mechanically milled  $GdAl_2$ , the magnetic behavior is not as simple. A glassy state exists below  $T_g$ , but its character is more complex. In addition, a simple Curie-Weiss equation is not sufficient to explain the high-temperature paramagnetic region.

## II. EXPERIMENTAL

The initial bulk sample of  $GdAl_2$  was fabricated by arc melting Gd (99.9%) shot with Al (99.999%) shot. The crystalline sample was then ground to a powder. Both of these fabrication methods took place in an argon atmosphere to reduce contamination of the sample. The sample powder was then annealed in a vacuum space of  $10^{-6}$  torr for 48 hours at 800 °C.

Initial x-ray diffraction measurements indicated that the starting material was in fact  $GdAl_2$ . Any impurity phases were below the resolution of the instrument.

After annealing, the sample was placed back in an argon atmosphere where it was milled within a tungsten-carbide-lined vial in a SPEX 8000 mixer/mill for up to 400 hours. This paper will focus on the 350-hour and 400-hour samples.

High temperature DC magnetization measurements were performed using a SQUID Magnetometer. DC magnetization measurements were performed on the 350-hour sample using fields of 50 and 100 Oe. Fields ranging from 1 – 1000 Oe were used for the 400-hour sample.

AC susceptibility ( $\chi'$  and  $\chi''$ ) measurements were performed using a Lakeshore 7225 susceptometer/magnetometer. AC measurements were taken for the 350-hour and 400-hour samples, using fields of 1 Oe and 10 Oe, and frequencies ranging from 5 to 500 Hz. AC measurements with an applied DC field were also performed on the 350-hour sample using an AC field of 1 Oe and 55 Hz, and DC bias fields of 100 Oe and 1 kOe.

### III. RESULTS & DISCUSSION

#### a. AC Susceptibility Measurements

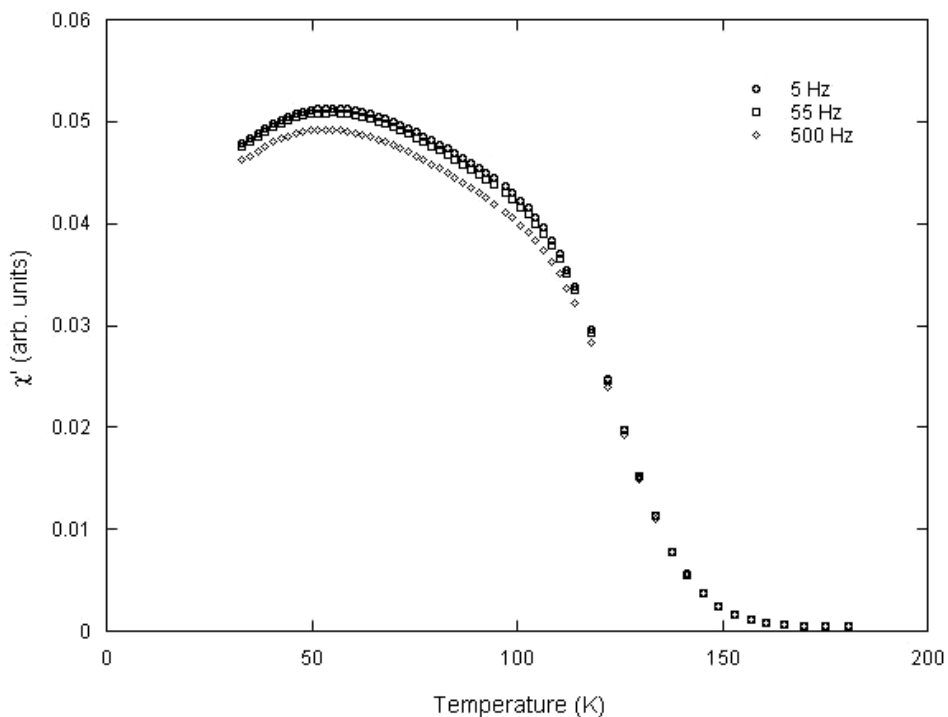
We will first look at standard AC susceptibility measurements (zero DC field). In Figures 1 and 2,  $\chi'$  and  $\chi''$  are shown for the 350-hour sample at a field strength of 1 Oe.  $\chi'$  represents the in-phase component of susceptibility while  $\chi''$  represents the out of phase component. Multiple frequencies are plotted on each graph. The magnitude of  $\chi'$  decreases as the frequency increases and vice versa for  $\chi''$ , as expected.  $\chi'$  shows a peak around 54 K and a slight shoulder around 98 K. The existence of a shoulder is even more pronounced in the plot of  $\chi''$ .  $\chi''$  peaks around 97 K and continues down to a shoulder at approximately 53 K. The close proximity of the shoulder and the peak in the susceptibility data makes it difficult to distinguish the nature of the two features and their frequency dependence. However, it is clear that the peak in  $\chi''$  shifts to higher temperatures as the frequency increases.

Figures 3 and 4 show plots of  $\chi'$  and  $\chi''$  for the 350-hour sample at a field strength of 10 Oe. The data follow similar behavior. In addition, there is no significant change in

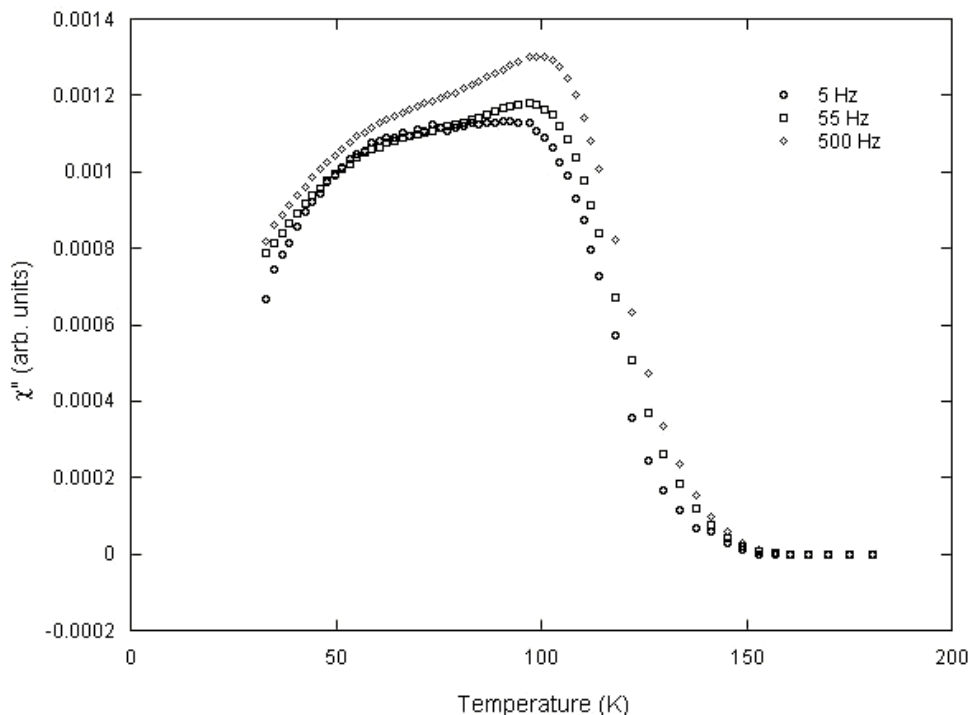
the magnitude of the data from a field of 1 Oe to 10 Oe. Similarly, there appears to be little to no temperature shift due to the change in AC field strength. Thus the AC susceptibility is independent of AC field strength up to 10 Oe.

Figs. 5 and 6 provide the same measurement for the 400-hour sample at 10 Oe. Although the data are noticeably more noisy, the same general behavior can be seen.

As suggested later, the peak in  $\chi''$  is ferromagnetic in nature and the lower shoulder is due to a glassy state. Because of this, we would expect there to be no frequency dependence for the peak in  $\chi''$  (as is characteristic of a bulk ferromagnet), which is not what is observed. If we assumed that the glassy state's frequency dependence was causing an apparent frequency dependence for the ferromagnetic component, the shift in the glassy peak of  $\chi'$  should be more pronounced than it is. In addition, the frequency dependence of the glassy phase would actually cause the ferromagnetic peak in  $\chi''$  to shift to lower temperatures as frequency increased, which is the opposite of what is observed.



**Figure 3.** AC Susceptibility of 350-hour sample  $\text{GdAl}_2$  at 10 Oe, showing the in-phase component of susceptibility as a function of temperature,  $\chi'$  vs. T.



**Figure 4.** AC Susceptibility of 350-hour sample  $\text{GdAl}_2$  at 10 Oe., showing the out-of-phase component of magnetic susceptibility as a function of temperature,  $\chi''$  vs. T.

However, it is quite clear that the ferromagnetic peak is unusually broad, spanning a range of approximately 50 K. This suggests that there is no bulk contribution to the ferromagnetic component [6]. A bulk contribution would consist of large domains that have an essentially infinite response time, leading to the lack of a frequency dependence and much sharper peak than seen in our data.

Milling for 400 hours produces a sample with a mean grain size of approximately 8 nm. This indicates that, although small, grains of crystalline  $\text{GdAl}_2$  are still present in the sample. Being the only contribution to a ferromagnetic component, these small ferromagnetic grains would have finite response times, leading to a possible ferromagnetic frequency dependence as well as a broadened peak.

#### b. AC Susceptibility Measurements With An Applied DC Field

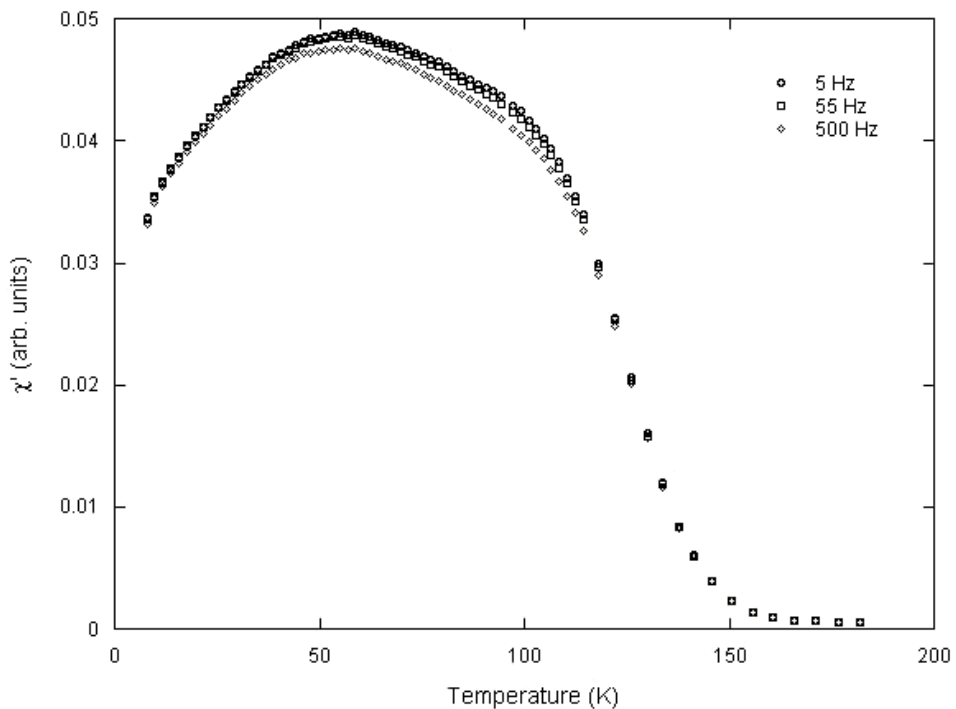
Applied DC measurements prove to be a strong method for suppressing the

ferromagnetic component of the magnetic behavior.

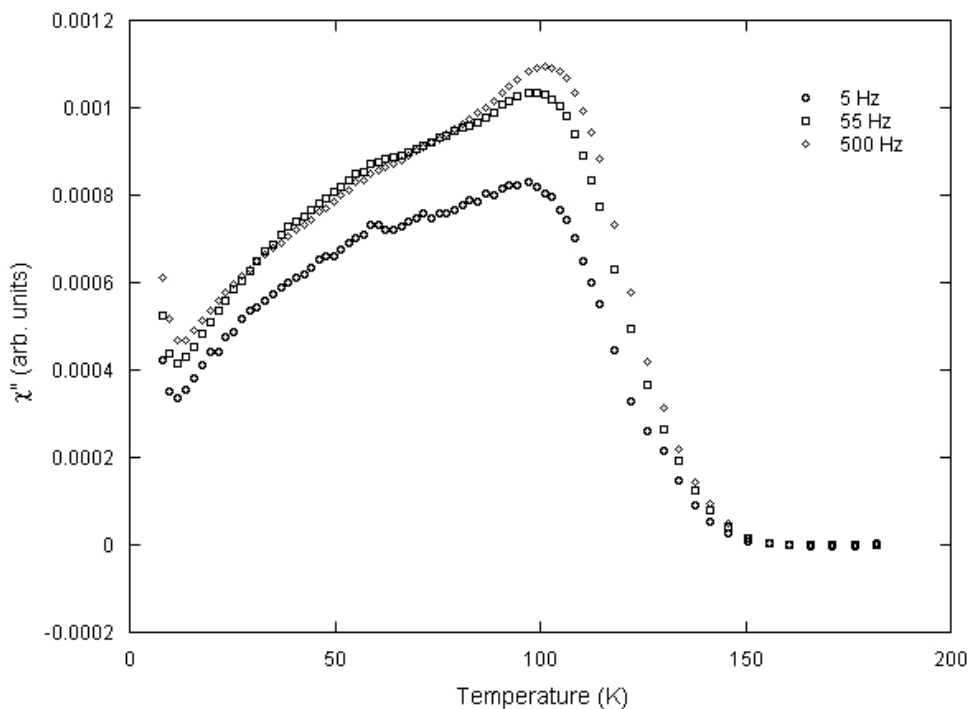
Due to restrictions on liquid He, only the 350-hour sample was investigated using the applied DC methods. Figures 7 and 8 show the applied DC measurements that were made using an AC field of 1 Oe and a frequency of 55 Hz. An applied DC field of 100 Oe and 1 kOe are plotted along with the original AC susceptibility (0 Oe DC).

With an applied DC field of 100 Oe, the shoulder around 98 K in  $\chi'$  is removed and the lower temperature peak becomes more refined. The peak then resembles that of a typical spin glass state, albeit less sharp. With a DC field of 1 kOe, the graph takes on a very different shape. It is evident that the DC field is strong enough to suppress the susceptibility of the glassy state at this value.

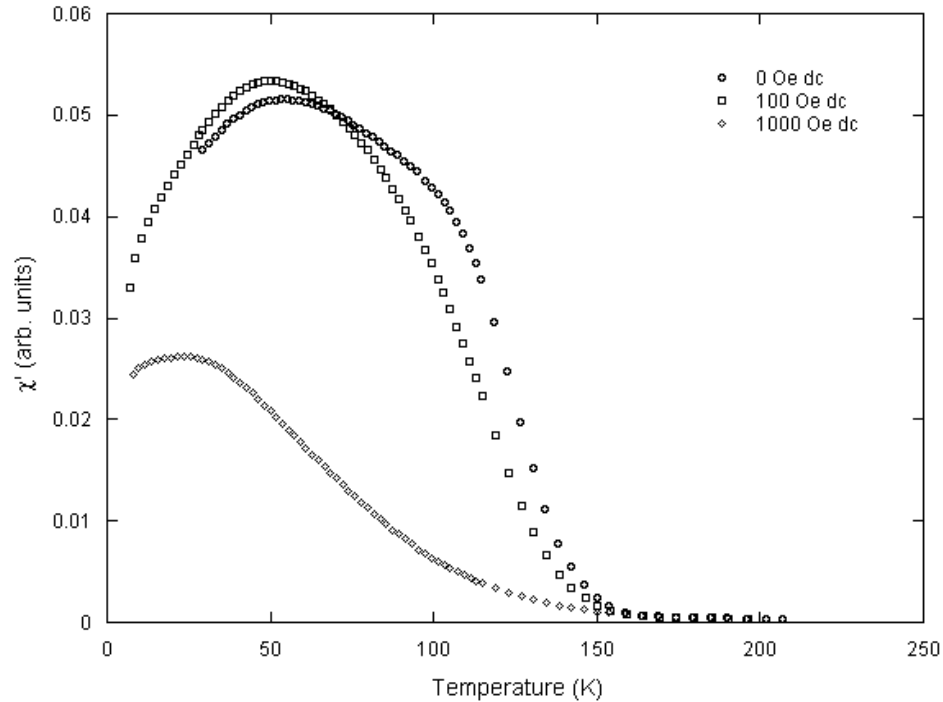
The effects of the applied DC field are even more evident in  $\chi''$ , as seen in Fig. 8. The sharp peak around 100 K has been completely removed with an applied DC field of 100 Oe. The lower temperature shoulder remains as a nice glassy peak. Again, 1 kOe DC seems to drastically



**Figure 5.** AC Susceptibility of 400-hour sample of  $GdAl_2$  at 10 Oe, showing the in-phase component of susceptibility as a function of temperature,  $\chi'$  vs. T.



**Figure 6.** AC Susceptibility of 400-hour sample of  $GdAl_2$  at 10 Oe., showing the out-of-phase component of magnetic susceptibility as a function of temperature,  $\chi''$  vs. T.



**Figure 7.** AC measurements of 350-hour sample of  $\text{GdAl}_2$  at 1 Oe AC and 55 Hz with an applied DC field, showing the in-phase component of susceptibility as a function of temperature,  $\chi'$  vs. T.

suppress the AC magnetic response. It is also important to note the dramatic upturn that occurs in  $\chi''$  at about 10 K. The majority of the measurements made previously did not extend down to this temperature and hence do not show this additional feature. Similarly,  $\chi'$  exhibits a downturn at the same temperature.

The AC susceptibility data and the applied DC data suggest behavior that resembles that of a reentrant spin glass [7]. The Sherrington-Kirkpatrick model of a reentrant spin glass allows for the coexistence of ferromagnetic and spin glass states [8]. However, we believe that multiple sources of magnetism are present in mechanically milled  $\text{GdAl}_2$ —one contributing to a strong ferromagnetic component and another contributing to a substantial glassy component.

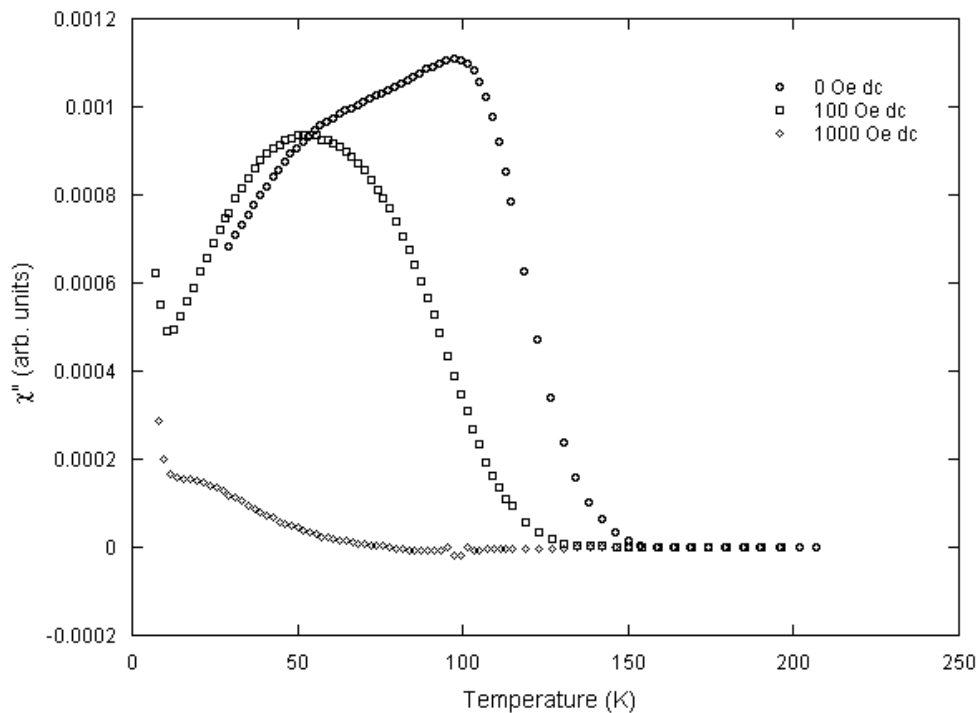
It is likely that the previously mentioned remaining ferromagnetic grains are the cause of the ferromagnetic component. The glassy component of the susceptibility can be attributed to the disordered interphase that separates each of the ferromagnetic grains. The upturn in

the low temperature  $\chi''$  data may be a signature of the freezing of the magnetizations of the grains, due to interactions between grain and interphase spins. Further testing will focus on this region, as it is necessary to more accurately determine the nature of this upturn. More support for the theory of multiple magnetic components follows.

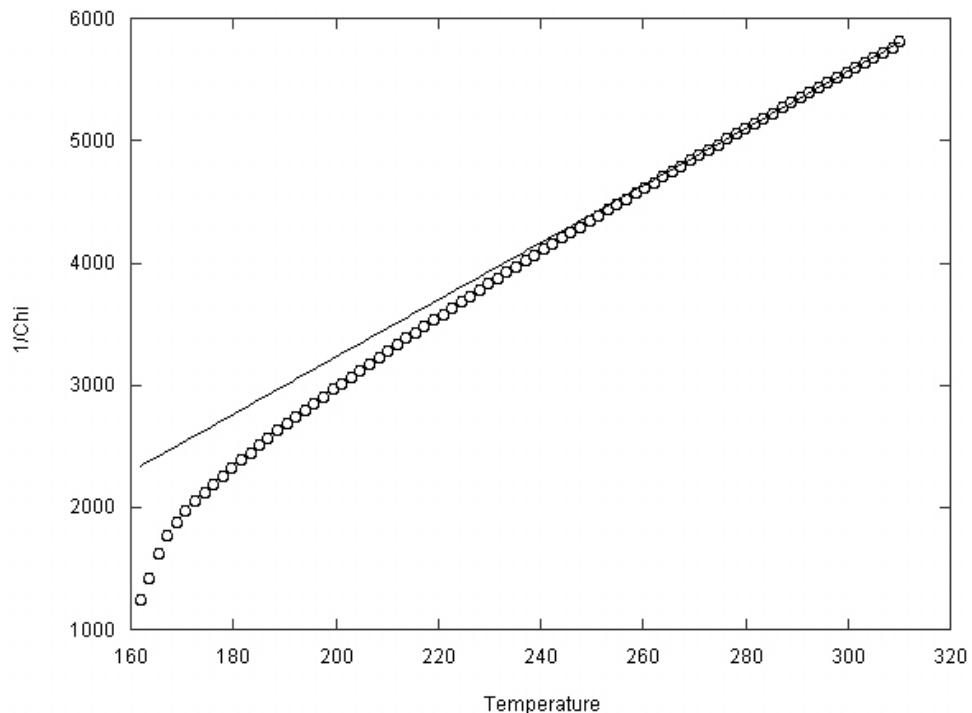
### c. High Temperature DC Measurements

Figure 9 shows a plot of  $\chi^{-1}$  for the DC magnetization measurements of the 350-hour sample. The high temperature data displays significant curvature in what is the paramagnetic region. A simple Curie-Weiss fit, obtained from the highest temperatures, is displayed along with the data to show the deviation from simple paramagnetic behavior. The downward curvature from the Curie-Weiss fit signifies that an antiferromagnetic component may be present.

We have suggested that two sources of magnetic behavior are present in the milled  $\text{GdAl}_2$ , a glassy component due to



**Figure 8.** AC measurements of 350-hour sample of  $GdAl_2$  at 1 Oe AC and 55 Hz with an applied DC field, showing the out-of-phase component of magnetic susceptibility as a function of temperature,  $\chi''$  vs. T.



**Figure 9.**  $\chi^{-1}$  vs. T for high temperature DC magnetization measurements with a single Curie-Weiss fit, with a 350-hour sample at 100 Oe.

the interphase and a ferromagnetic component due to the unmilled grains at low temperatures. Both of these components would undergo a transition to a paramagnetic phase at their respective ordering temperatures, giving rise to a superposition of Curie-Weiss fits. Considering this, Figures 10 and 11 show a “double Curie-Weiss fit” for the same data. The fit was obtained using a *Mathematica* program and the general equation is as follows:

$$\chi = C_1/(T-\theta_1) + C_2/(T-\theta_2)$$

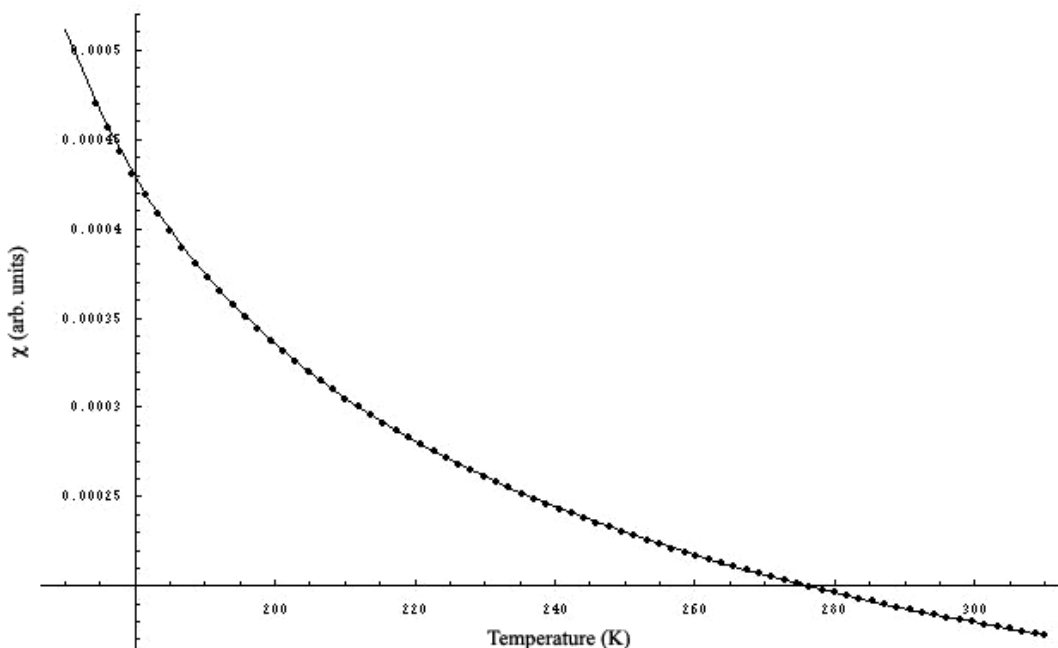
Any constant, temperature-independent susceptibility terms, such as diamagnetic, Pauli paramagnetic, or instrumental background effects, were taken to be negligible, as they are orders of magnitude less than other susceptibility contributions. As seen in Figure 11, the fit follows the curvature of  $\chi^{-1}$  very well. In addition, Figure 10 shows that the dramatic upturn in  $\chi$  around 175 K is also well represented. The fit seems to follow the entire range of the high temperature data quite well. The best fit had a sum of the squares of deviance equal to  $4.86 \times 10^{-12}$  and is shown below:

$$\chi = 0.0104193 / (T - 136.626) + 0.0357296 / (T + 9.09292)$$

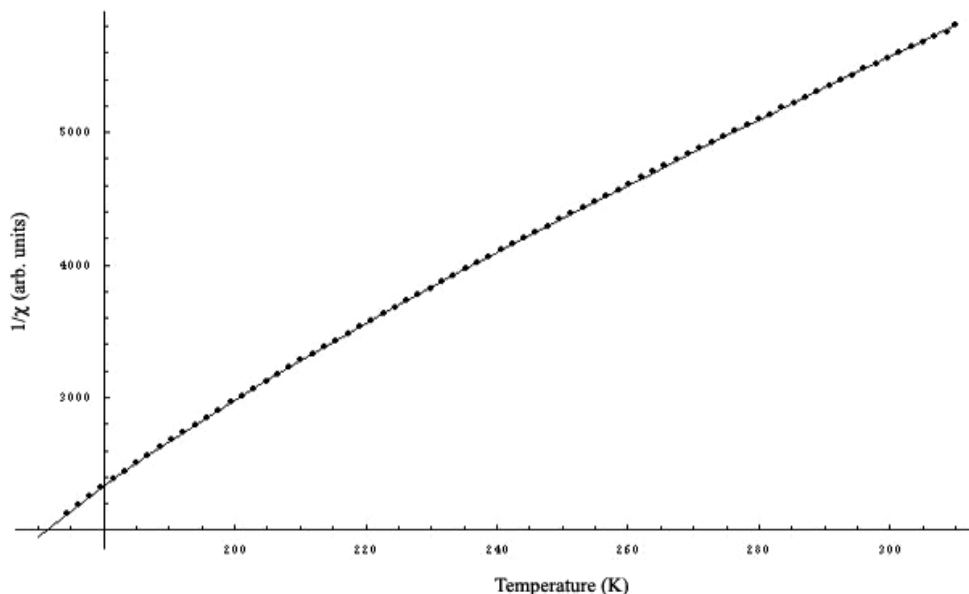
It turns out that the best fit occurs for slightly negative values of  $\theta_2$ , as shown. This indicates that the glassy phase undergoes a transition at  $T_g$  to a paramagnetic phase that is slightly antiferromagnetic in nature.

The fit also indicates that the ferromagnetic component has a Curie-Weiss temperature  $\theta_1 \approx 137$  K. As  $T$  approaches  $\theta_1$ , the ferromagnetic component dominates the Curie-Weiss behavior, thereby producing the downturn in the  $\chi^{-1}$  vs.  $T$  plot.

It is interesting to note that the fit suggests the ferromagnetic component is the minority component. Since  $C_1 < C_2$ , it follows that  $N_1 p_{eff,1}^2 < N_2 p_{eff,2}^2$ . If we assume that  $p_{eff,1} \approx p_{eff,2}$ , then  $N_1$  must be less than  $N_2$ . Therefore, the disordered interphase and greatly disordered grains are likely the dominant contributor to the magnetic behavior of the sample, responsible for the low-temperature glassy state. The minority ferromagnetic state is most likely due to small remnant ferromagnetic grains with little disorder.



**Figure 10.** Double Curie-Weiss fit of the 350-hour sample of GdAl<sub>2</sub> at 100 Oe DC, showing  $\chi$  vs.  $T$ .



**Figure 11.** Double Curie-Weiss fit of the 350-hour sample of  $\text{GdAl}_2$  at 100 Oe DC, showing  $\chi^{-1}$  vs. T.

#### IV. CONCLUSION

Measurements of DC susceptibility, AC susceptibility, and AC susceptibility with an applied DC bias field were performed on mechanically milled  $\text{GdAl}_2$ . The measurements show a magnetically glassy state at lower temperatures and a paramagnetic state at higher temperatures, both of which deviate from typical behavior. AC measurements with an applied DC bias field reveal a strong ferromagnetic component coexisting with the glassy component. With the ferromagnetic component suppressed, the glassy cusp resembles that of a spin glass. Fits to the high temperature DC data show that two Curie-Weiss terms provide a good fit for the data.

All measurements indicate that more than one magnetic component may be present in the mechanically milled sample of  $\text{GdAl}_2$ .

Future work will focus on probing the glassy phase more extensively by suppressing the ferromagnetic component with an applied DC bias field. The frequency and field dependence of the glassy phase can then be determined. Also, we plan to investigate the upturn in  $\chi''$  at low temperatures.

In addition, further milling is necessary to ascertain how the separate magnetic components evolve with increased milling time.

#### ACKNOWLEDGEMENTS

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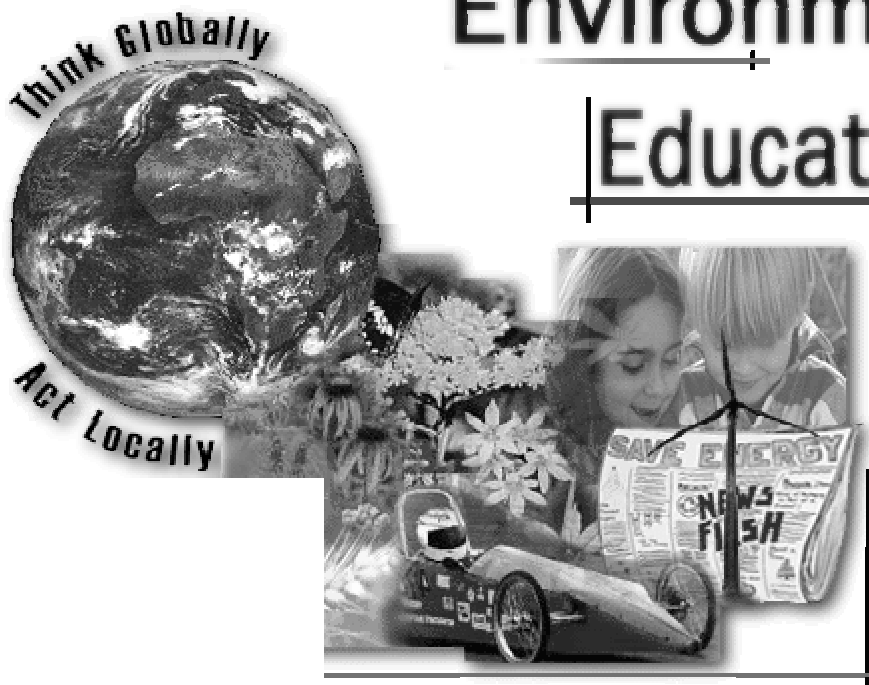
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