Static Critical Behavior of the Spin-Freezing Transition in the Geometrically Frustrated Pyrochlore Antiferromagnet Y$_2$Mo$_2$O$_7$

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The past five years have seen a resurgence of significant interest devoted to the systematic study of geometrically frustrated antiferromagnets [1,2]. Geometric frustration arises in materials containing antiferromagnetically coupled magnetic moments which reside on geometrical units, such as triangles and tetrahedra, that inhibit the formation of a collinear magnetically ordered state. One of the main motivations for the current interest in these systems stems from suggestions that the increased propensity of frustrated antiferromagnets for quantum zero-temperature spin fluctuations compared to collinear antiferromagnets might be sufficient to destroy Néel order and drive these systems into novel quantum disordered ground states [1,2].

Systems of classical Heisenberg spins residing on lattices of corner-sharing triangles or tetrahedra and antiferromagnetically coupled via nearest-neighbor exchange constitute particularly interesting cases of highly frustrated antiferromagnets. Here, theory [3–5] and numerical work [4,5] show that these systems do not order and remain in a “collective paramagnetic state” [3] down to zero temperature. Since, even for classical spins, these systems have such a small tendency to order, they are excellent candidates for displaying exotic quantum disordered ground states [2,6]. However, and perhaps most interestingly, experiments show that some nominally perfect (i.e., disorder-free) [7] pyrochlore antiferromagnetic lattices of corner-sharing tetrahedra exhibit a spin-freezing transition at some temperature $T_f$ [8], below which they develop magnetic irreversibilities (see Fig. 1) and long-time magnetic relaxation similar to what is found in conventional randomly frustrated spin-glasses such as CuMn, EuSrS, and CdMnTe [9]. Muon spin relaxation measurements also find a large increase of the $1/T_1$ muon depolarization rate at $T \approx 20$ K, and which indicates a dramatic critical slowing down of the Mo$^{4+}$ moments [10].

Two important questions arise: Firstly, what is the microscopic origin of the glassy behavior in pyrochlore antiferromagnets? Is it due to the yet undetected microscopic disorder inherent to any real material, or is it intrinsic to the idealized perfect material? Secondly, irrespective of the origin of the glassy behavior, one would like to know if the spin freezing is strictly dynamical (i.e., where the system’s relaxation time exceeds the time scale set by the experimental probe), or is it due to an underlying thermodynamic transition characterized by a truly divergent (spin-glass) correlation length and time scale as is believed to occur in conventional disordered spin glasses [9]? To address these two questions, we have measured the nonlinear magnetic susceptibility, $\chi_{nl}$, of the pyrochlore antiferromagnet Y$_2$Mo$_2$O$_7$. Briefly, we have found (i) that the freezing at $T_f$ is well characterized as a thermodynamic transition displaying a power-law divergence of the nonlinear susceptibility coefficient $\chi_3(T) \sim (T - T_f)^{-\gamma}$ with $\gamma \approx 2.8$, and that the net nonlinear susceptibility, $\chi_{nl}$, exhibits critical behavior and temperature-field scaling properties close to $T_f$ which gives a critical exponent, $\beta = 0.8$. The values we obtain for $\gamma$ and $\beta$ are typical of those found in conventional disordered spin-glasses, despite any obvious microscopic

![FIG. 1. Field-cooled (FC, squares) and zero field-cooled (ZFC, triangles) susceptibility for Y$_2$Mo$_2$O$_7$ in a magnetic field 100 Oe.](image_url)
disorder in $Y_2Mo_2O_7$ [7]. Previous high temperature measurements of the susceptibility in the Curie-Weiss regime, $\chi = C/(T - \theta)$ show that $\theta \sim -200$ K, with a Curie constant $C$ giving an effective magnetic moment of the order of 2.3 Bohr magneton per Mo$^{4+}$ [11]. This is very close to the theoretically expected value of 2.8 Bohr magneton per Mo$^{4+}$. Measurements of the high temperature susceptibility performed on our samples over the range 10–800 K are fully consistent with these earlier results. $Y_2Mo_2O_7$ therefore consists of a dense system of Mo$^{4+}$ moments.

$Y_2Mo_2O_7$ is a narrow band gap semiconductor, where the Mo$^{4+}$ ions are magnetic, with an antiferromagnetic nearest-neighbor Mo-Mo superexchange, while Y$^{3+}$ is diamagnetic. The 270 mg powder sample of Y$_2$Mo$_2$O$_7$ was prepared as described in Ref. [7]. Neutron and x-ray powder diffraction refinement analysis of our sample showed that there was no measurable amount of oxygen vacancies or intermixing between the Y$^{4+}$ and the Mo$^{4+}$ sublattices [7]. The random disorder in that material, most likely oxygen vacancies, is therefore below the 1% detectability level. The magnetization was measured using a commercial SQUID (Quantum Design, San Diego) magnetometer. The bulk magnetization of $Y_2Mo_2O_7$ becomes history dependent below $T_f = 22$ K: The field-cooled (FC) and zero field-cooled (ZFC) magnetizations measured in a field of 100 Oe show a sharp breakaway, as is found in conventional spin-glasses [9], below $T_f = 22$ K (see Fig. 1) [7].

To determine whether or not a true thermodynamic spin-freezing transition occurs around $T_f = 22$ K in $Y_2Mo_2O_7$, we have measured the nonlinear susceptibility coefficient, $\chi_3(T)$, which is expected to show a power-law critical divergence at $T_f$ [9]:

$$\chi_3 \propto \tau^{\gamma}, \quad (1)$$

with $\tau = T/T_f - 1$ and $\gamma > 0$. $\chi_3$ is extracted from the temperature, $T$, and field, $H$, dependence of the magnetization, $M(T, H) = \chi_1(T)H - \chi_3(T)H^3 + \chi_5(T)H^5 - \ldots$, where $\chi_1(T)$ is the linear susceptibility. Hence, the temperature dependence of $\chi_3(T)$, allows a determination of $T_f$ and $\gamma$ [9]. In fact, all the nonlinear terms $\chi_{2n+1}$ with $n \geq 1$ must diverge at $T_f$, since both $M(T, H)$ and $H$ are finite quantities. It is therefore convenient to define a net nonlinear susceptibility, $\chi_{n\text{lin}}$, as $\chi_{n\text{lin}}(T, H) \equiv 1 - M(T, H)/\chi_1(H)$. Right at $T_f$, $\chi_{n\text{lin}}$ has a power-law dependence on $H$:

$$\chi_{n\text{lin}}(T = T_f, H) \sim H^{2/d}, \quad (2)$$

where $d$ is a second independent static critical exponent characterizing the spin-freezing transition [9]. Finally, perhaps the most relevant test ascribing critical behavior to a spin-freezing transition is obtained by seeking a scaling behavior of $\chi_{n\text{lin}}$ of the form

$$\chi_{n\text{lin}}(T, H) \propto H^{2/d} \mathcal{F}(\tau^{(\gamma + \beta)/2}/H), \quad (3)$$

where $\beta$ is the spin-glass order parameter critical exponent [9]. Here, $\mathcal{F}(x)$ is the scaling function which must obey the following asymptotic behavior: $\mathcal{F}(x) = \text{const}$ for $x \to 0$, and $\mathcal{F}(x) \propto x^{-2\gamma/(\gamma + \beta)}$ for $x \to \infty$, in order that the scaling behavior has “physical content” [12], and that Eqs. (1) and (2) are recovered [9,12], hence, giving the scaling relation

$$\delta = 1 + \gamma/\beta. \quad (4)$$

The magnetization data were obtained under field-cooling conditions. The field, $H$, in the range 100–7000 Oe, was switched on at high temperature ($70$ K $\sim 3T_f$), and kept constant during subsequent slow cooling at a rate 5 mK/s in a fixed field, and down to the temperature of interest. It took over an hour to go from 70 K to any of the $(H,T)$ data points presented in our paper. The reason we cooled down in fixed field instead of working along conventional isotherms is to eliminate any possibility of a magnetic field hysterisis of the superconducting magnet in the magnetometer affecting the results; the magnetic field was never decreased during the whole experiment. Because of the irreversible and time-dependent nature of the system’s response below $T_f$, only results in the temperature range $T_f < T < 3T_f$ are included. Our results on the dynamical relaxation of the magnetization in $Y_2Mo_2O_7$ at $T < T_f$ will be reported elsewhere.

Prior to doing any analysis, we have to deal with the fact that the interactions do not perfectly average to zero, as evidenced by $\chi_1(T)$ not having a simple $\chi_1 \sim 1/T$ Curie law. It has been argued [9,13] that the leading (first-order) corrections to scaling coming from this nonzero averaging of the interactions can be eliminated by fitting $M(T,H)/H$ to powers of $a_{2n+1}(T)\chi_1[H^{2n}]$ for $n \geq 0$, instead of simply $\chi_{2n+1}H^{2n}$, and considering the critical behavior of $a_{2n+1}(T)$ instead of $a_{2n+1}(T)$. For each temperature the field dependence of $M(T,H)/H$ at small field was fitted with $M(T,H)/H = \chi_1 - \chi_3H^2$, giving $a_3 = \chi_3/\chi_1$, and varying the upper limit of the field range to determine the limit of validity of this restricted fit beyond which higher $\chi_{2n+1}$ ($n > 1$) corrections become significant. The quality of our magnetization data did not allow us to determine the $a_5 = \chi_5/\chi_1^5$ coefficient with precision better than (50–100)%, and thus $a_5$ data are not included here. We show in Fig. 2 the net nonlinear susceptibility, $\chi_{n\text{lin}}(T,H)$, with $\chi_1$ extracted from the fit $M(T,H)/H = \chi_1 - \chi_3H^2$, as a function of $H^2$ for few temperatures above $T_f$. These results emphasize the large increase of $\chi_{n\text{lin}}$ upon approaching $T_f$. We also notice that $\chi_{n\text{lin}}$ is only linear in $H^2$ up to a maximum field $H_{s}(T)$ whose value is rapidly moving to zero upon approaching $T_f$ due to the turning on of the $\chi_{2n+1}$ ($n > 1$) corrections which themselves diverge at $T_f$ as $\tau^{(\beta-n\gamma)/\beta}$ [9].

Figure 3 shows a log-log plot of $\chi_3/\chi_1$ vs $T/T_f - 1$ for five different choices of $T_f$. The steepness of the
curves increases as the chosen value for $T_f$ is decreased. Choosing $T_f > 23.0$ would result in a curve with essentially no extended range of power-law behavior ($\chi_3/\chi_1 \propto \tau^{-\gamma}$). Also, values of $T_f > 23.0$ K are definitely above the FC-ZFC breakaway point where the magnetization data acquisition runs are reversible at the lowest field [7,8]. Values of $T_f < 21.0$ are also not easy to justify as they are clearly well below the FC-ZFC break-away point at $=22$ K. Also, one observes an obvious upward curvature at the far left of the data with the choice $T_f = 21.0$ K. Consequently, the log-log plot of the $\chi_3/\chi_1$ data strongly suggests that $T_f$ is finite and between 21.0 K and 23.0 K, and the extracted value of $\gamma$ depends on the choice of $T_f$. To better quantify this, we have fitted $\chi_3/\chi_1 \propto (1 - T/T_f)^{-\gamma}$ for a fixed range of values $\chi_3/\chi_1 \in [2-30]$ (i.e., for a fixed number of data points) giving the solid line fits in Fig. 3. The goodness of fit, $X^2 = \sum [(a_3^{calc}(\tau_i) - a_3^{meas}(\tau_i))^2$, with $a_3 = \chi_3/\chi_1^3$ and $\tau_i = T_i/T_f - 1$, versus the choice of $T_f$ is shown in the inset of Fig. 3, along with the corresponding variation of the critical exponent $\gamma$. As can be seen, a pronounced minimum in $X^2$ is seen as a function of $T_f$, and the best fit is obtained for $T_f = 22.2$ K, which gives a value $\gamma = 2.8$. Overall, a conservative estimate gives $T_f \in [21.7-22.7]$ K, giving $\gamma \in [2.4-3.4]$. The power-law divergence of $a_3 = \chi_3/\chi_1^3$ saturates for $\tau < 0.05$ for a choice of $T_f \in [22.0-23.0]$ K. A reason for this leveling off of $a_3$ is that the range of dominance of the term $\chi_3(T)H^2$ to $\chi$ falls below the smallest field, $H_{\text{min}}(H_{\text{min}} \sim 100$ Oe), for which good quality data were obtained. The increasingly important diverging higher-order terms of alternating signs ($\chi_5, \chi_7, \text{etc.}$) contributing to $\chi_{nl}$ then cause $a_3$ to be underestimated when $H(T)$ becomes less than or equal to $=H_{\text{min}}$. Also, the slow but finite cooling rate inhibits the correct equilibrium value of $\chi_{nl}$ from being attained, and this effect may be compounded with the previous one to produce a saturation of $a_3$ for $t < 0.05$. Overall, the observed behavior of $a_3$ for $Y_2\text{Mo}_2\text{O}_7$ seen in Fig. 3 as well as the uncertainty on the value of $\gamma$ are typical of what is observed in conventional, chemically disordered spin-glasses.

We now attempt to verify that the spin freezing in $Y_2\text{Mo}_2\text{O}_7$ is a legitimate critical phenomenon by seeking a data collapse and scaling behavior of the net nonlinear susceptibility of the form given in Eq. (3). Choosing $T_f = 22.2$ K and $\gamma = 2.8$, as found in the inset of Fig. 3, we can find a reasonable data collapse (scaling) of $\chi_{nl}$ with a choice of $\beta = 0.75 \pm 0.10$ (see Fig. 4).
Working with other choices of $T_f \in [21.7-22.7]$ K, and $\gamma \in [2.4-3.4]$, we find $\beta \in [0.6-0.9]$. As found for $\gamma$ above, such a value for $\beta$ is typical of that found in conventional disordered spin-glasses [9]. The scatter of the data at large $x$, $x = \tau^{(y+\beta)/2}/H$, arises because these data are those that correspond to relatively high temperature (well above $T_f$) and small fields, where the nonlinear magnetization is small and the experimental error is the largest. In the limit $x \to 0$, we observe that $\tilde{F}(x)$ approaches a constant value, hence confirming that $\chi_{fl} \propto H^{2/\delta}$ at $T = T_f$ with Eq. (4) obeyed. Taking $\gamma = 2.8$ and $\beta = 0.75$ at $T = T_f = 22.2$ K, Eq. (4) predicts a value $\delta = 4.73$. The inset of Fig. 4 shows a log-log plot of $\chi_{fl}(T = T_f = 22.2) K vs H$ with this value of $\delta = 4.73$ (solid line). The fit is very good, confirming that the collapse of the $\chi_{fl}(T, H)$ data has physical meaning underlying a critical phenomenon which fulfills Eq. (4). Also, in the limit of large $x$ (i.e., at small fields), we observe that the asymptotic behavior of $\tilde{F}(x)$ is consistent with the power-law $\tilde{F}(x) \propto x^{-2y/(y+\beta)}$ (dashed line in main panel of Fig. 4) as, again, it should be for the data collapse to have physical meaning and such that $\chi_{fl} \sim \tau^{-\gamma}H^{2\delta}$ for $T \gg T_f$ and $H \to 0$.

It is interesting to compare our results for the $Y_2Mo_2O_7$ pyrochlore with those for the SrCr$_5$Ga$_4$O$_{19}$ kagomé system (SCGO) [2,12,14], and for the site-ordered gadolinium gallium garnet magnet Gd$_5$Ga$_{4}O_{12}$ (GGG) [2,15]. Ramirez et al. [14] found a power-law divergence of $\chi_3$ in SCGO with $\gamma = 2.4$, while Martinez et al. [12] recently argued that the freezing at $T_f \approx 3.5$ K in SCGO is not associated with a divergence of $\chi_3$ ($\chi_3$ was found to increase by a factor of 5 or so in Ref. [12]), and that this material does not exhibit conventional spin-glass behavior. Also, contrary to what we find for $Y_2Mo_2O_7$, Martinez et al. argued that the data collapse (i.e., scaling behavior) they obtained for $\chi_{fl}$ of SCGO was “unphysical” since the asymptotic behavior of their scaling function was inconsistent with what it should have been according to the scaling relation $\delta = 1 + \gamma/\beta$ [12]. Schiffer et al. [15] found a large increase of $\chi_3$ in GGG (6 orders of magnitude between 0.2 K and 5 K), which they ascribe to a spin-glass transition. However, the temperature dependence of $\chi_3$ in GGG is qualitatively different than what is found in conventional spin-glasses where $\chi_3$ has two maxima in GGG, while it is a monotonic function of the temperature in conventional spin-glasses as well as here in $Y_2Mo_2O_7$. Hence, from the point of view of nonlinear susceptibility measurements, it therefore appears that the spin-glass behavior observed in $Y_2Mo_2O_7$ resembles much more closely what is found in conventional spin-glasses than that which has been found in other geometrically frustrated antiferromagnets, such as SCGO and GGG.

In conclusion, we have measured the nonlinear dc susceptibility of the nominally disorder-free geometrically frustrated pyrochlore antiferromagnet $Y_2Mo_2O_7$ close to and above the spin-freezing temperature, $T_f \sim 22$ K, where this material shows spin-glass behavior. Our results show that the freezing transition observed in $Y_2Mo_2O_7$ is well characterized by a power-law divergence of the $\chi_3(T)$ nonlinear susceptibility coefficient, $\chi_3(T) \propto (T/T_f - 1)^{-\gamma}$, with a value $\gamma \sim 2.9 \pm 0.5$. This implies an underlying thermodynamic glass phase transition around 22 K in this material. This is further supported by recent muon spin relaxation measurements [10]. The net nonlinear susceptibility data, $\chi_{fl}(T > T_f, H)$, can be collapsed onto a scaling function from which we can extract the order parameter critical exponent $\beta \sim 0.8 \pm 0.2$. Right at $T_f$, we find a behavior $\chi_{fl} \sim H^{2/\delta}$ with a value of $\delta \sim 4.7$, which satisfies the scaling relation $\delta = 1 + \gamma/\beta$ [Eq. (4)]. The values we find for $\gamma$, $\beta$, and $\delta$ are typical of those found in conventional chemically disordered spin-glasses [9].

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