Static Critical Behavior of the Spin-Freezing Transition in the Geometrically Frustrated Pyrochlore Antiferromagnet $Y_2Mo_2O_7$

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Some frustrated pyrochlore antiferromagnets, such as $Y_2Mo_2O_7$, show a spin-freezing transition and magnetic irreversibilities below a temperature T_f similar to what is observed in *randomly* frustrated spin-glasses. We present results of nonlinear dc magnetization measurements on $Y_2Mo_2O_7$ that provide strong evidence that there is an underlying thermodynamic phase transition at T_f, which is characterized by critical exponents $\gamma \approx 2.8$ and $\beta \approx 0.8$. These values are typical of those found in random spin-glasses, despite the fact that the level of random disorder in $Y_2Mo_2O_7$ is immeasurably small. [S0031-9007(96)02232-6]

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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, $\chi_{\rm nl}$, of the pyrochlore antiferromagnet $Y_2Mo_2O_7$. 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, $\chi_{\rm nl}$, exhibits critical behavior and temperature-field scaling properties close to T_f which gives a critical exponent, $\beta \approx 0.8$. The values we obtain for γ and β are typical of those found in conventional disordered spin-glasses, despite any obvious microscopic

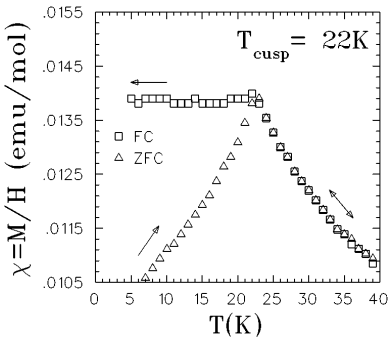

FIG. 1. Field-cooled (FC, squares) and zero field-cooled (ZFC, triangles) susceptibility for $Y_2Mo_2O_7$ in a magnetic field 100 Oe.

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 $Y_2Mo_2O_7$ 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^{3+} 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 $T_f \approx 22$ 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 $T_f \approx 22$ K (see Fig. 1) [7].

To determine whether or not a true thermodynamic spin-freezing transition occurs around $T_f \approx 22$ 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]:

$$\chi_3 \propto \tau^{-\gamma}, \tag{1}$$

with $\tau \equiv T/T_f - 1$ and $\gamma > 0$. χ_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 γ [9]. In fact, all the nonlinear terms χ_{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, $\chi_{\rm nl}$, as $\chi_{\rm nl}(T,H) \equiv 1 - M(T,H)/(\chi_1 H)$. Right at T_f, $\chi_{\rm nl}$ has a power-law dependence on H:

$$\chi_{\rm nl}(T = T_f, H) \sim H^{2/\delta}, \tag{2}$$

where δ 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 $\chi_{\rm nl}$ of the form

$$\chi_{\rm nl}(T,H) \propto H^{2/\delta} \mathcal{F}(\tau^{(\gamma+\beta)/2}/H), \tag{3}$$

where β 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

$$\delta = 1 + \gamma/\beta\,. \tag{4}$$

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 hysteresis 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 $a_{2n+1}(T)\chi_1[\chi_1 H]^{2n}$ for $n \geq 0$, instead of simply $\chi_{2n+1}H^{2n}$, and considering the critical behavior of $a_{2n+1}(T)$ instead of $\chi_{2n+1}(T)$. For each temperature the field dependence of $M(T,H)/H$ at small field was fitted with $M(T,H)/H = \chi_1 - \chi_3 H^2$, giving $a_3 = \chi_3/\chi_1^3$, and varying the upper limit of the field range to determine the limit of validity of this restricted fit beyond which higher χ_{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, $\chi_{\rm nl}(T,H)$, with χ_1 extracted from the fit $M(T,H)/H = \chi_1 - \chi_3 H^2$, as a function of H^2 for few temperatures above T_f. These results emphasize the large increase of $\chi_{\rm nl}$ upon approaching T_f. We also notice that $\chi_{\rm nl}$ is only linear in H^2 up to a maximum field $H_+(T)$ whose value is rapidly moving to zero upon approaching T_f due to the turning on of the χ_{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 χ_3/χ_1^3 vs $T/T_f - 1$ for five different choices of T_f. The steepness of the

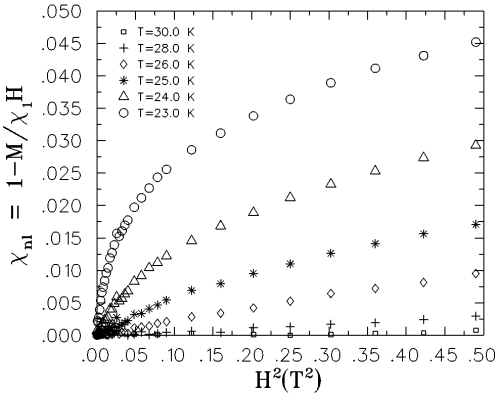

FIG. 2. Net nonlinear susceptibility, $\chi_{\rm nl} = 1 - M/\chi_1 H$ vs H^2 for the six temperatures indicated.

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 ($\chi_3/\chi_1^3 \propto \tau^{-\gamma}$). 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 $T_f = 21$ K. Consequently, the log-log plot of the χ_3/χ_1^3 data strongly suggests that T_f is finite and between 21.0 K and 23.0 K, and the extracted value of γ depends on the choice of T_f. To better quantify this, we have fitted $\chi_3/\chi_1^3 \propto (1 - T/T_f)^{-\gamma}$ for a fixed range of values $\chi_3/\chi_1^3 \in [2-30]$ (i.e., for a *fixed* number of data points) giving the solid line fits in Fig. 3. The goodness of fit, $X^2 = \sum_i [a_3^{\rm calc}(\tau_i) - a_3^{\rm meas}(\tau_i)]^2$, 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 γ. 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 $T_f \approx 22.2$ K, which gives a value $\gamma \approx 2.8$. 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 $\chi_{\rm nl}$ falls below the smallest field, $H_{\rm min}$($H_{\rm min} \sim 100$ Oe), for which good quality data were obtained. The increasingly important diverging higher-order terms of alternating signs (χ_5, χ_7, etc.) contributing to $\chi_{\rm nl}$ then cause a_3 to be underestimated when $H_+(T)$ becomes less than or equal to $\approx H_{\rm min}$. Also, the slow but finite cooling rate inhibits the correct equilibrium value of $\chi_{\rm nl}$ 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 $Y_2Mo_2O_7$ seen in Fig. 3 as well as the uncertainty on the value of γ are typical of what is observed in conventional, chemically disordered spin-glasses.

We now attempt to verify that the spin freezing in $Y_2Mo_2O_7$ 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 $\chi_{\rm nl}$ with a choice of $\beta = 0.75 \pm 0.10$ (see Fig. 4).

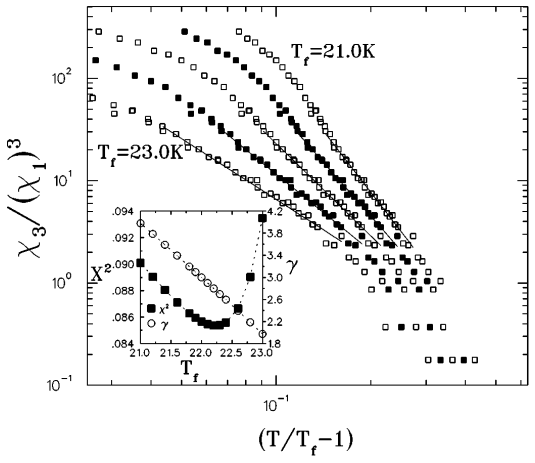

FIG. 3. Log-log plot showing the temperature dependence of $a_3 = \chi_3/\chi_1^3$ vs $\tau \equiv T/T_f - 1$ for five different choices of T_f: $T_f = 21.0$, 21.5, 22.0, 22.5, and 23.0 K. The inset shows the goodness of fit parameters, X^2 (filled squares), for the solid line fits in the main panel, and the exponent γ (open circles) vs the chosen value for T_f (see comments in text).

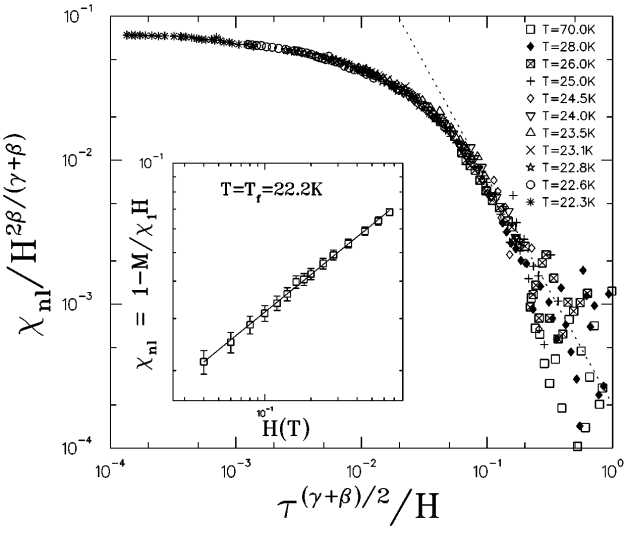

FIG. 4. Nonlinear magnetization analyzed according to a scaling model for a nonzero spin-glass transition temperature with choices $T_f = 22$ K, $\gamma = 2.8$, and $\beta = 0.75$. The inset shows the log-log plot of $\chi_{\rm nl}(T = T_f, H) \propto H^{2/\delta}$ with the value of $\delta = 4.73$ predicted from the scaling relation (4), with the values of $\gamma = 2.8$ and $\beta = 0.75$.

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 γ above, such a value for β is typical of that found in conventional disordered spin-glasses [9]. The scatter of the data at large x, $x \equiv \tau^{(\gamma+\beta)/2}/H$, 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 $\mathcal{F}(x)$ approaches a constant value, hence confirming that $\chi_{\rm nl} \propto H^{2/\delta}$ 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 $\delta \approx 4.73$. The inset of Fig. 4 shows a log-log plot of $\chi_{\rm nl}(T = T_f = 22.2)$ K vs H with this value of $\delta = 4.73$ (solid line). The fit is very good, confirming that the collapse of the $\chi_{\rm nl}(T, H)$ 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 $\mathcal{F}(x)$ is consistent with the power-law $\mathcal{F}(x) \propto x^{-2\gamma/(\gamma+\beta)}$ (dashed line in main panel of Fig. 4) as, again, it should be for the data collapse to have physical meaning and such that $\chi_{\rm nl} \sim \tau^{-\gamma} H^2$ 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 $SrCr_8Ga_4O_{19}$ kagomé system (SCGO) [2,12,14], and for the site-ordered gadolinium gallium garnet magnet $Gd_3Ga_5O_{12}$ (GGG) [2,15]. Ramirez *et al.* [14] found a power-law divergence of χ_3 in SCGO with $\gamma \approx 2.4$, 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 χ_3 (χ_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 $\chi_{\rm nl}$ 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 χ_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 χ_3 in GGG is qualitatively different than what is found in conventional spin-glasses since χ_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, $\chi_{\rm nl}(T > T_f, H)$, 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 $\chi_{\rm nl} \sim H^{2/\delta}$ with a value of $\delta \sim 4.7$, which satisfies the scaling relation $\delta = 1 + \gamma/\beta$ [Eq. (4)]. The values we find for γ, β, and δ are typical of those found in conventional chemically disordered spin-glasses [9].

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