Nonlinear susceptibility measurements at the spin-glass transition of the pyrochlore antiferromagnet $Y_2Mo_2O_7$

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We have measured the magnetic field and temperature dependence of the nonlinear dc susceptibility, $\chi_{\rm nl}$, of the frustrated pyrochlore antiferromagnet $Y_2Mo_2O_7$ close to and above the temperature, $T_g \sim 22$ K, where this material exhibits irreversible (spin-glass like) magnetic behavior. Our results suggest that the observed irreversible magnetic properties in this material are due to a thermodynamic spin-glass transition signaled by a divergence of the nonlinear magnetic susceptibility coefficient $\chi_3 \sim (T/T_g - 1)^{-\gamma}$ at T_g with $\gamma = 3.3 \pm 0.5$. $\chi_{\rm nl}$ shows *two* power-law behavior at T_g, $\chi_{\rm nl} \sim H^{2/\delta}$, with $\delta \sim 2.8$ for $H < 1000$ Oe and $\delta \sim 4.1$ for $H > 2000$ Oe. These values for γ and δ, as well as the crossover behavior of $\chi_{\rm nl}$ at T_g, is consistent what is found in common disordered Heisenberg spin glass materials. © *1996 American Institute of Physics.* [S0021-8979(96)23908-4]

The study of magnetic materials with competing, or *frustrated*, antiferromagnetic interactions, inhibiting the formation of a collinear magnetically ordered state, goes back more than forty years.[1,2] However, the past five years have seen considerable increase in the number of systematic experimental, theoretical, and numerical investigations of these systems.[2,3] For example, it has been suggested that the phase transition into a noncollinear spin structure may belong to a ''new'' chiral universality class different from the universality classes appropriate to collinear magnets.[4] Also, the proposal that large levels of frustration can generate quantum zero-point spin fluctuations sufficient to destroy Néel order at zero temperature even for two and three-dimensional systems, and lead to novel types of magnetic ground states, has attracted much attention.[2,3]

Several families of insulating antiferromagnetic materials with extreme frustration level have been identified.[3] Examples include the kagomé and pyrochlore systems. In the kagomé $SrCr_xGa_{12-x}O_{19}$ (Ref. 5) and $KM_3(OH)_6(SO_4)_2$ (Ref. 6) (M=Cr or Fe) materials, the moment carrying cations (Cr, Fe) reside on stacked, two-dimensional lattices of corner sharing triangles.[5,6] In the $A_2B_2O_7$ pyrochlores (A =Y,Tb; B=Mn,Mo), the A^{3+} and B^{4+} cations, which can be either magnetic or nonmagnetic, sit on two distinct, interpenetrating lattices of corner-sharing tetrahedra.[7–10]

In both the classical kagomé and pyrochlore Heisenberg antiferromagnets, the elementary triangular or tetrahedral plaquettes are highly frustrated, and the classical ground state of the system is determined by the quite unrestrictive condition $\Sigma_{i\in\Delta}\mathbf{S}_{i,\Delta}=0$ on *each* individual plaquette Δ, where $\mathbf{S}_{i,\Delta}$ is a classical spin on lattice site i of plaquette Δ. The number of states which satisfy this local condition increases exponentially with system size, leading to a finite ground state entropy per spin, and a *collective* paramagnetic ground state.[7] In real systems, however, perturbations such as lattice distortions, crystal-field effects, further nearest-neighbor exchange or dipolar coupling can lead to the selection of a classical Néel ordered ground state.[7,8] A mechanism of order-by-disorder via thermal or quantum fluctuations may also be at play, and lead to long-range order.[8] One may therefore expect two generic scenarios for real kagomé and pyrochlore antiferromagnets. They could display long-range Néel order, possibly with a sizeable quantum reduction of the staggered moment due to the ''fragility'' of the classical order brought about solely by perturbative effects.[8,11] Alternatively, quantum fluctuations may be sufficiently large to destabilize the otherwise classical ground state, and drive the system to an unconventional quantum ground state.[2,11] It is therefore interesting that a large number of kagomé[3,5,6] and pyrochlore[9,10] antiferromagnets fail to display long-range, or even extended short-range, Néel order. Instead, they exhibit magnetic irreversibilities, i.e., spin-glass like behavior, below a glass temperature, T_g.[9,10] This is surprising as a large number of these systems can be prepared with a very high degree of chemical and structural purity.[9,10] The mechanism responsible for this spin-glass behavior is not understood, and is currently the subject of an intense debate.[12] However, irrespective of the origin of the glassiness, one would still like to know: ''Does T_g correspond to a true thermodynamic phase transition or, alternatively, is it a dynamical freezing transition?''

$Y_2Mo_2O_7$ 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. 9. Neutron and x-ray powder diffraction studies show that there is no measurable amount of oxygen vacancies or intermixing between the Y^{3+} and the Mo^{4+} sublattices.[9] Any random disorder in that material is therefore below the 1% detectability level. The magnetization was measured using a SQUID magnetometer. The bulk magnetization of $Y_2Mo_2O_7$ becomes hysteretic below $T_g \approx 22$ K: the field-cooled (FC) and zero field-cooled (ZFC) magnetizations measured in fields of 100 Oe show a sharp

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breakaway below 22 K.[9] This is a characteristic signature of the freezing transition observed in conventional chemically disordered spin glass materials.[13]

To assess whether or not a true thermodynamic spin-glass phase transition occurs 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 close to T_g of the type $\chi_3 \sim (T-T_g)^{-\gamma}$ ($\gamma>0$). [13] χ_3 is extracted from the temperature, T, and field, H, dependence of the magnetization, $M(T,H)$,

$$M(T,H)=\chi_1(T)H-\chi_3(T)H^3+\chi_5(T)H^5-\ldots, \tag{1}$$

where $\chi_1(T)$ is the linear susceptibility. Hence, the temperature dependence of $\chi_3(T)$ allows a determination of T_g and γ.[13] In fact, all the nonlinear terms χ_{2n+1} with $n \geqslant 1$ must diverge at T_g, since both $M(T,H)$ and H are finite quantities. It is therefore convenient to define a "full" nonlinear susceptibility, $\chi_{\rm nl}$, as

$$\chi_{\rm nl}(T,H) \equiv 1-\frac{M(T,H)}{\chi_1 H}. \tag{2}$$

Right at T_g, $\chi_{\rm nl}$ has a power law dependence on H:

$$\chi_{\rm nl}(T_g,H) \sim H^{2/\delta}, \tag{3}$$

where δ is a second critical exponent characterizing the spin-glass transition.[13]

The magnetization data were collected using the SQUID magnetometer under field-cooling conditions; the field H, in the range 100–7000 Oe was switched on at high temperature (70 K$\sim 3T_g$), and kept constant during subsequent slow cooling at a rate 5 mK/s down to the temperature of interest. Because of the irreversible and time-dependent nature of the system's response below T_g only results in temperature range $T_g<T<3T_g$ are included. Our results on the low-temperature dynamical relaxation of the magnetization in $Y_2Mo_2O_7$ will be reported elsewhere.[14] Three consecutive cooling runs for fixed field were performed, with the magnetization data averaged over the three runs.

Figure 1(a) shows the field cooled susceptibility $\chi(T,H) \equiv M(T,H)/H$ for six different cooling fields. Prior to doing any analysis, we dealt with the fact that the interactions do not perfectly average to zero, as evidenced by the fact that $\chi_1(T)$ does not have a simple $\chi_1 \sim 1/T$ Curie law. The *leading* corrections to scaling coming from this nonzero averaging of the interactions can be eliminated by fitting $\chi(T,H)$ in powers of $a_{2n+1}(T)\chi_1[\chi_1 H]^{2n}$ for $n \geqslant 0$, instead of simply $\chi_{2n+1}H^{2n}$, and considering the critical behavior or $a_{2n+1}(T)$ instead of $\chi_{2n+1}(T)$.[13] For each temperature the field dependence of χ at small field was fitted with $\chi=\chi_1-\chi_3 H^2$, 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 these a_5 data are not included here. We show in Fig. 1(b) the full nonlinear susceptibility, $\chi_{\rm nl}(T,H)$, as defined in Eq. (2), with χ_1 extracted from the fit $\chi(T,H)=\chi_1-\chi_3 H^2$, as a function of H^2 for a few temperatures above T_g. These results emphasize the

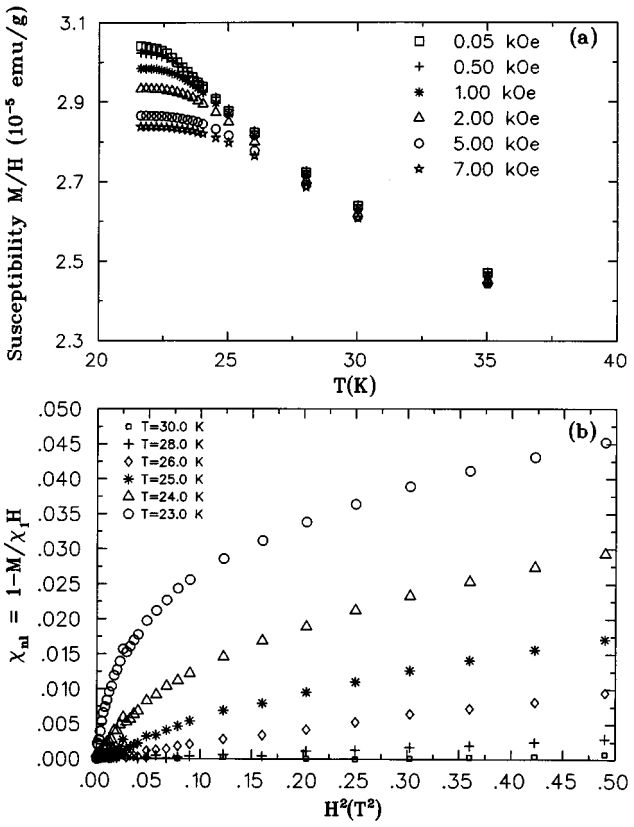

FIG. 1. Panel (a): Raw data, susceptibility M/H vs T for six different cooling fields. Panel (b): net nonlinear susceptibility, $\chi_{\rm nl}=1-M/\chi_1 H$ vs H^2 for the six temperatures indicated.

large increase of the nonlinear susceptibility upon approaching T_g in this material. We also notice that the $\chi_{\rm nl}$ is only linear in H^2 up to a maximum field $H_+(T)$ whose value is rapidly moving to $H_+(T)=0$ upon approaching T_g. This is due to the turning on of the χ_{2n+1} ($n>1$) corrections which diverge at T_g as $(T-T_g)^{(\beta-n[\gamma+\beta])}$.[13]

Figure 2(a) shows a log-log plot of a_3 versus T/T_g-1 with $T_g=21.8$ K. There are two sets of data shown on this figure, the squares and the triangles. The two data sets were obtained with the same $Y_2Mo_2O_7$ sample, but from two separate set of experiments separated by four months. The excellent agreement in the absolute value of a_3 between the two sets of experiments (i.e., no vertical or horizontal shifting of one set with respect to the other was done) gives us an estimate of the precision of our measurements. A power-law fit to the data with square symbols resulted in a fit with minimum χ^2 value for $T_g=21.9$ K, yielding a critical exponent $\gamma=3.3\pm0.5$. A fit for the triangles give a best fit for $T_g=21.7$ K with a critical exponent of also $\gamma=3.3\pm0.5$. The power-law divergence of a_3 saturates for $t<0.07$ ($t \equiv T/T_g-1$). A reason for this levelling off of a_3 for $t<0.07$ is that the range of dominance of the term $\chi_3(T)H^2$ to $\chi_{\rm nl}$ falls below the smallest field, $H_{\rm min}$ ($H \sim 100$ Oe), for which reliable data are available to us. 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 or equal to $\approx H_{\rm min}$. Another possible effect may be the slow but finite cooling rate inhibits the attainment of

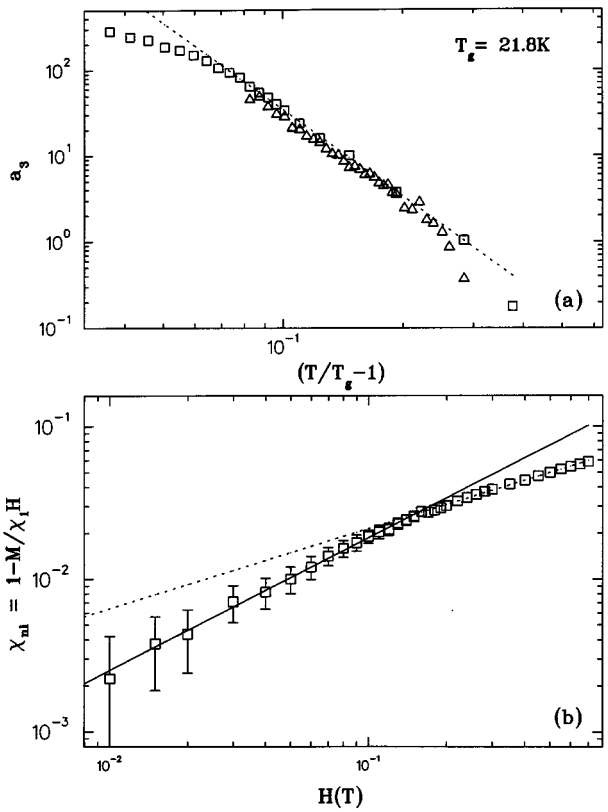

FIG. 2. Panel (a): log-log plot showing the temperature dependence of $a_3(T)$. The square and triangular symbols correspond to two set of independently analyzed experiments. The dashed line shows the power law fit to the square symbols with the average $T_g=21.8$ K. Panel (b): log-log plot of the net nonlinear susceptibility, $\chi_{\rm nl}$, vs applied field H at $T=21.8$ K. The dashed and solid lines correspond to power-law fits for fields $H<1000$ Oe and $H>2000$ Oe, respectively (see discussion in text).

the correct equilibrium value of $\chi_{\rm nl}$ and this effect is compounded with the previous one, saturating a_3 for $t<0.07$. Figure 2(b) shows a log-log plot of $\chi_{\rm nl}$ versus H at $T_g=21.8$ K for fields $H=100-7000$ Oe. At criticality, one expects that $\chi_{\rm nl}$ will be given by Eq. (3), with a single value of δ for fields $H\ll J$, where J is the rms value of the superexchange interactions. Clearly, we observe two trends in Fig. 3(b), one for small fields and one for large fields, with a crossover field between the two regimes of the order of $H_{\rm co}\approx 1500$ Oe. The value of δ is found to be 2.8 ± 0.5 for $H<1000$ Oe (dashed line) and 4.1 ± 0.1 for $H>2000$ Oe (solid line). Such field induced crossover, with similar values of $\delta(H<H_{\rm co})$ and $\delta(H>H_{\rm co})$ has also been seen in conventional disordered spin glasses.[13]

It is interesting to compare our results for the $Y_2Mo_2O_7$ pyrochlore with those of the $SrCr_8Ga_4O_{19}$ kagomé system (SCGO),[15,16] and for the site-ordered gadolinium gallium garnet magnet $Gd_3Ga_5O_{12}$ (GGG).[17] Ramirez *et al.*[15] found a power-law divergence of χ_3 in SCGO with $\gamma\approx 2.4$, while Martinez *et al.*[16] recently published results where they argue 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 5 or so in Ref. 16), and that this material does not exhibit conventional spin glass behavior. Schiffer *et al.*[17] found a large increase of χ_3 in GGG (6 orders of magnitude between 0.2 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. Hence, from the point of view of nonlinear susceptibility measurements, it appears that the spin glass behavior observed in $Y_2Mo_2O_7$ resembles much more what is found in conventional spin glasses than what has been found in other topologically frustrated antiferromagnets, such as SCGO and GGG.

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