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

M.J.P. Gingras$^{1,*}$, C.V. Stager$^2$, N.P. Raju$^3$, B.D. Gaulin$^2$, and J.E. Greedan$^3$

$^1$TRIUMF, Theory Group, 4004 Wesbrook Mall, Vancouver, B.C., V6T-2A3, Canada
$^2$Department of Physics and Astronomy, McMaster University, Hamilton, ON L8S 4M1, Canada
$^3$Department of Chemistry, McMaster University, Hamilton, ON L8S 4M1, Canada

(July 23, 2018)

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 DC nonlinear 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.

*Present address: Department of Physics, University of Waterloo, Waterloo, ON, N2L 3G1, Canada

PACS:75.50.Ee, 75.50.Lk, 75.40.Cx

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. The main motivation for the current interest in these systems stems from suggestions that (i) they may display critical phenomena belonging to a “new” chiral universality class different from the universality classes of collinear magnets [2, 3], or (ii) 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 non-classical quantum disordered ground states [4, 5].

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 (see Fig. 1). Here, theory [2, 3] and numerical work [6], show that these systems do not order and remain in a “collective paramagnetic state” down to zero temperature. Since, even for classical spins, these systems have such a small tendency to order, they are excellent candidates to display exotic quantum disordered ground states [5]. However, and perhaps most interestingly, experiments show that some nominally perfect (i.e. disorder-free) pyrochlore antiferromagnets [10] exhibit a spin-freezing transition at some temperature $T_f$, 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 [11].

FIG. 1. The top figure shows the field-cooled (FC, squares) and zero field-cooled (ZFC, triangles) magnetization for $Y_2Mo_2O_7$ in a magnetic field 1000Oe. The bottom figure shows the three-dimensional network of corner-sharing tetrahedra formed by the Mo$^{4+}$ sublattice in $Y_2Mo_2O_7$.

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 [1]? To address these two questions, we have measured the nonlinear magnetic susceptibility, $\chi_{nl}$, 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, $\chi_{nl}$, 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 $\gamma$ and $\beta$ are typical of those found in conventional disordered spin glasses, despite any obvious microscopic disorder in $Y_2Mo_2O_7$ [3]. High temperature measurements of the susceptibility in the Curie-Weiss regime, $\chi = C/(T - \theta)$ show that $\theta \sim -200K$, with a Curie constant $C$ giving an effective magnetic moment of the order of 2.5 Bohr magneton per Mo$^{4+}$ [2]. This is very close to the theoretically expected value of 2.8 Bohr magneton per Mo$^{4+}$. We have recently performed high temperature susceptibility measurements in the range 10K–800K which are in agreement with Hubert’s results [3]. Clearly, these indicate that the susceptibility, and thereby the spin-glass behavior observed in $Y_2Mo_2O_7$ is not due to a small fraction of the spins, but arises from the very large majority of the moments. Essentially, $\chi$ is small close to $T_f = 23K$ because $\theta$ is so large and since $Y_2Mo_2O_7$ is an antiferromagnet (i.e. $\theta$ is negative).

$Y_2Mo_2O_7$ 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. Figure 1 shows the cubic unit cell of the Mo$^{4+}$ magnetic lattice where there is a magnetic Mo moment on the vertices of the tetrahedra. The 270mg powder sample of $Y_2Mo_2O_7$ was prepared as described in Reference 1. 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 [4]. 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 $T_f \approx 22K$: the field-cooled (FC) and zero field-cooled (ZFC) magnetizations measured in a field of 1000Oe show a sharp breakaway below 22K (see Fig. 1) [4].

To determine whether or not a true thermodynamic spin-freezing transition occurs around $T_f = 22K$ 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 $T_f$ [4]:

$$\chi_3 \propto \tau^{-\gamma} ,$$  \hspace{1cm} (1)

with $\tau \equiv T/T_f - 1$ 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 $\gamma$ [4]. 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, $\chi_{nl}$, as

$$\chi_{nl}(T, H) \equiv 1 - \frac{M(T, H)}{\chi_1H} .$$ \hspace{1cm} (2)

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

$$\chi_{nl}(T = T_f, H) \sim H^{2/\delta} ,$$ \hspace{1cm} (3)

where $\delta$ is a second independent static critical exponent characterizing the spin-freezing transition [4]. Finally, and perhaps the most relevant test ascribing critical behavior to the spin-freezing transition is obtained by seeking a scaling behavior of $\chi_{nl}$ of the form

$$\chi_{nl}(T, H) \propto H^{2/\delta} F((\gamma + \beta)/2, H) ,$$ \hspace{1cm} (4)

in order that the scaling behavior has “physical content” [5], and that Eqs. 3 and 4 are recovered [3,6], hence giving the scaling relation

$$\delta = 1 + \gamma/\beta .$$ \hspace{1cm} (7)

The magnetization data were obtained under field-cooling conditions. The field $H$, in the range $[100 - 7000]$Oe, was switched on at high temperature ($70K \sim 3T_f$), 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 70K to any of the $(H - T)$ data point presented in our paper. This means almost twelve hours to get to the lowest temperature. 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 low temperature dynamical relaxation of the magnetization in Y$_2$Mo$_2$O$_7$ will be reported elsewhere. Three consecutive cooling runs for fixed field were performed, with the magnetization data averaged over the three runs.

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 [3,15] several times that the leading (first-order) corrections to scaling coming from this non-zero averaging of the interactions can be eliminated by fitting $\chi(T, H)$ 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 $\chi_{2n+1}(T)$. For each temperature the field dependence of $\chi$ at small field was fitted with $\chi = \chi_1 - \chi_2 H^2$, giving $a_2 = \chi_3/\chi_1$, 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, $\chi_{nl}(T, H)$, as defined in Eq. (4), with $\chi_1$ extracted from the fit $M(T, H)/H = \chi_1 - \chi_2 H^2$, as a function of $H^2$ for few temperatures above $T_f$. These results emphasize the large increase of the nonlinear susceptibility upon approaching $T_f$. We also notice that $\chi_{nl}$ is only linear in $H^2$ up to a maximum field $H_\perp(T)$ 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 $\tau^{(3-n(\gamma+\beta))}$ [11].

Figure 3 shows a log-log plot of $\chi_3/\chi_1^3$ 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 give us a curve with essentially no extended range of power-law behavior ($\chi_3/\chi_1 \propto \tau^{-\gamma}$). As can be seen in the top of Fig. 1, values of $T_f > 23.0$K are definitely above the FC-ZFC break-away point where the magnetization data acquisition runs are reversible at the lowest field. Values of $T_f < 21.0$ are also not possible to justify as they are clearly well below the FC-ZFC break-away point. Also, one observes an obvious upward curvature at the far left of the data with the choice $T_f = 21K$. Consequently, the log-log plot of the $\chi_3/\chi_1^3$ data strongly suggests that $T_f$ is finite and between 21.0K and 23.0K, and the extracted value of $\gamma$ 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 value $\chi_3/\chi_1^3 \in [2 - 30]$ for a fixed number of data points (solid line fits on Fig. 3). The goodness-of-fit, $X^2 = \sum (a_i^{calc}(\tau_i) - a_i^{meas}(\tau_i))^2$, with $a_3 = \chi_3/\chi_1^3$ and $\tau_i = 1 - T_i/T_f$ vs 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 $T_f \approx 22.2K$, which gives a value $\gamma \approx 2.8$. Overall, a conservative estimate gives $T_f \in [21.7 - 22.7]K$, giving $\gamma \in [2.4 - 3.4]$.  

![Figure 2](image-url)  

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

![Figure 3](image-url)  

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

The power-law divergence of $a_3 = \chi_3/\chi_1^3$ saturates for $T/T_f$ = 0.05 for a choice of $T_f \in [22.0 - 23.0]K$. A reason for
this levelling off of \( a_3 \) is that the range of dominance of the term \( \chi_3(T)H^2 \) to \( \chi_{nl} \) falls below the smallest field, \( H_{\text{min}} \) (\( H_{\text{min}} \sim 100\text{Oe} \)), 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 \( \approx H_{\text{min}} \). 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. 4. Choosing \( T_f = 22.2\text{K} \) 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 \( \beta = 0.75 \pm 0.10 \). Had we worked with other choices of \( T_f \in [21.7 - 22.7]\text{K} \), and \( \gamma \in [2.4 - 3.4] \), we would have found \( \beta \in [0.6 - 0.9] \). As found for \( \gamma \) above, such a value for \( \beta \) is typical of that found in conventional disordered spin glasses [11]. The scatter of the data at large \( x, x \equiv \tau^{(\gamma+\delta)/2}/H \), 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 \( F(x) \) approaches a constant value, hence confirming that \( \chi_{nl} \propto H^{2/\delta} \) at \( T = T_f \) with Eq. 4 obeyed. Taking \( \gamma = 2.8 \) and \( \beta = 0.75 \) at \( T = T_f = 22.2\text{K} \), Eq. 4 predicts a value \( \delta \approx 4.73 \). The inset of Fig. 4 shows a log-log plot of \( \chi_{nl}(T = T_f = 22.2)\text{K} \) vs \( H \) with this value of \( \delta = 4.73 \) (solid line). The fit is very good, confirming that the collapse of the \( \chi_{nl}(T, H) \) data has physical meaning underlying a critical phenomenon which obeys Eq. 4. Also, in the limit of large \( x \) (i.e. at small fields), we observe that the asymptotic behavior of \( F(x) \) is consistent with the power-law \( F(x) \propto x^{-2\gamma/(\gamma+\delta)} \) (dashed-line in main panel of Fig. 4) as, again, it should be for the data collapse to have physical meaning and such that \( \chi_{nl} \sim \tau^{-\gamma}H^2 \) for \( T \gg T_f \) and \( H \to 0 \).

It is interesting to compare our results for the \( Y_2\text{Mo}_2\text{O}_7 \) pyrochlore with those for the SrCr$_2$Ga$_4$O$_{19}$ kagomé system (SCGO) [14,15], and for the site-ordered gadolinium garnet magnet Gd$_3$Ga$_5$O$_{12}$ (GGG) [16]. Ramirez et al. [16] found a power-law divergence of \( \chi_3 \) in SCGO with \( \gamma \approx 2.4 \), while Martínez et al. [14] recently argued that the freezing at \( T_f \approx 3.5\text{K} \) in SCGO is not associated with a divergence of \( \chi_3 \) (\( \chi_3 \) was found to increase by a factor 5 or so in Ref. [14]), and that this material does not exhibit conventional spin glass behavior. Also, contrary to what we find for \( Y_2\text{Mo}_2\text{O}_7 \), Martínez et al. argued that the data-collapse (i.e. scaling behavior) they obtained for the net nonlinear susceptibility 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 \( \delta = 1+\gamma/\beta \) [14]. Schiffer et al. [17] found a large increase of \( \chi_3 \) in GGG (6 orders of magnitude between 0.2K and 5K), 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 since \( \chi_3 \) has two maxima in GGG, while it is a monotonic function of the temperature in conventional spin glasses as well as here in \( Y_2\text{Mo}_2\text{O}_7 \). Hence, from the point of view of nonlinear susceptibility measurements, it therefore appears that the spin glass behavior observed in \( Y_2\text{Mo}_2\text{O}_7 \) resembles more closely what is found in conventional spin glasses than that which has been found in other topologically frustrated antiferromagnets, such as SCGO and GGG. 

![FIG. 4. Nonlinear magnetization analyzed according to a scaling model for a nonzero spin-glass transition temperature with choices \( T_f = 22.2\text{K} \), \( \gamma = 2.8 \) and \( \beta = 0.75 \). The inset shows the log-log plot of \( \chi_{nl}(T = T_f, H) \propto H^{2/\delta} \) with the value of \( \delta = 4.73 \) predicted from the scaling relation Eq. 4, with the values of \( \gamma = 2.8 \) and \( \beta = 0.75 \).](image-url)
In conclusion, we have measured the nonlinear DC susceptibility of the pyrochlore antiferromagnet Y$_2$Mo$_2$O$_7$ close to and above the freezing temperature, $T_f \sim 22$K, where this material shows spin-glass behavior. Our results show that the freezing transition observed in Y$_2$Mo$_2$O$_7$ is well characterized by a power law divergence of the $\chi_3(T)$ nonlinear susceptibility coefficient, $\chi_3(T) \propto (1 - T/T_f)^{-\gamma}$, with a value $\gamma \sim 3.0 \pm 0.5$. This implies an underlying thermodynamic glass phase transition around 22K in this material. This is further supported by recent muon spin relaxation measurements where a large increase of the $1/T_1$ muon depolarization rate at $T \approx 20$K has been observed, and which indicate a dramatic critical slowing down of the Mo$^{4+}$ moments [18]. The net nonlinear susceptibility data, $\chi_{nl}(T > T_f, H)$, 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 $\chi_{nl} \sim H^{2/\delta}$ with a value of $\delta \sim 4.7$, which satisfies the scaling relation [15]. The values we find for $\gamma$ and $\beta$ are typical of what is found in conventional chemically disordered spin glasses [16].

We hope that our results will stimulate further experimental and theoretical studies to clarify the origin of the spin-freezing transition and the low-temperature glassiness seen in Y$_2$Mo$_2$O$_7$ and other geometrically frustrated magnetic systems.

We thank D. Huse, A. Ramirez and G. Williams for useful discussions, and M. Harris for allowing us to use his postscript figure of the pyrochlore lattice structure. This research has been funded by the NSERC under the NSERC Collaborative Research Grant Geometrically-Frustrated Magnetic Materials.

---

[1] J.M.D. Coey, Can. J. Phys. 65, 1210 (1987).
[2] Magnetic systems with competing interactions, ed. H.T. Diep, (World Scientific, Singapore, 1994); P. Chandra and P. Coleman, New Outlooks and Old Dreams in Quantum Antiferromagnets, Les Houches Summer School Lectures (August 1991).
[3] A.P. Ramirez, Annu. Rev. Mater. Sci. 24, 453 (1994); P. Schiffer and A.P. Ramirez, Comments Cond. Mat. Phys. 18, 21 (1996); B.D. Gaulin and M.J.P. Gingras, to appear in J. Phys. Cond. Matt.
[4] H. Kawamura, in Recent Advances in Magnetism of Transition Metal Compounds, eds. A. Kotani and N. Suzuki, (World Scientific, Singapore, 1993); ibid., J. Phys. Soc. Jpn. 61, 1299 (1992) and references therein.
[5] J. Villain, Z. Phys. B 33, 31 (1978).
[6] J.N. Reimers, A.J. Berlinsky, and A.-C. Shi, Phys. Rev. B 43, 865 (1991); J.N. Reimers, Phys. Rev. B 45, 7287 (1992); M. Kvale (unpublished).
[7] J.N. Reimers, Phys. Rev. B 45, 7287 (1992); J.T. Chalker, P.C.W. Holdsworth and E.F. Shender, Phys. Rev. Lett., 68, 855 (1992). J.N. Reimers and A.J. Berlinsky, Phys. Rev. B 48, 9539 (1993).
[8] R.R.P. Singh and D.A. Huse, Phys. Rev. Lett. 68, 1766 (1992); J.T. Chalker and J.F.G Eastmont, Phys. Rev. B 46, 14201 (1992).
[9] J.E. Greedan et al., Solid State Commun. 59, 895 (1986); J.N. Reimers and J.E. Greedan, J. Solid State Chem. 72, 390 (1988); N.P. Raju, E. Gmelin, and R.K. Kremer, Phys. Rev. B 46, 5405 (1992).
[10] J.N. Reimers et al., Phys. Rev. B 43, 3387 (1991); J.E Greedan et al., ibid 43, 5682 (1991); B.D. Gaulin et al., Phys. Rev. Lett. 69, 3244 (1992).
[11] K. Binder and A.P. Young, Rev. Mod. Phys. 58, 801 (1986); K.H. Fischer and J.A. Hertz, Spin Glasses, (Cambridge University Press, Cambridge, 1991).
[12] Ph.-H. Hubert, Bull. Chem. Soc. France, 2385 (1974).
[13] N.P. Raju et al. (unpublished).
[14] B. Martinez et al., Phys. Rev. B 50, 15779 (1994).
[15] R. Omari, J.J. Prejean and J. Souletie, J. de Phys. 44, 1069 (1983); I. Yeung, R.M. Roehko and G. Williams, J. Magn. Mag. Mater. 68, 39 (1987); H. Bouchiat, J. de Physique 47, 71 (1986).
[16] A.P. Ramirez et al., Phys. Rev. Lett. 64, 2070 (1990).
[17] P. Schiffer et al., Phys. Rev. Lett. 74, 2379 (1995).
[18] S. Dunsiger et al., J. Appl. Phys., 79, 6636 (1996).
[19] Disorder-free spin-glassiness in pyrochlores and in the related two-dimensional kagomé Heisenberg antiferromagnet, has been much discussed in the past four years. See Refs. [1-10] and E.F. Shender et al., Phys. Rev. Lett. 70, 3812 (1993); V.B. Cherepanov (unpublished, 1994).