# Neutron-diffraction study of magnetic ordering in the pyrochlore series $R_2 Mo_2 O_7$ (R = Nd, Tb, Y)

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 $Nd_2Mo_2O_7$ ,  $Y_2Mo_2O_7$ , and  $Tb_2Mo_2O_7$  are all ordered crystalline oxides with the cubic pyrochlore structure. At 53 K,  $Nd_2Mo_2O_7$  is long-range ordered with a ferrimagnetic structure. A transition temperature of 95 K is determined from small-angle-neutron-scattering (SANS) data. Antiferromagnetic structures are proposed below 20 K that are consistent with previous magnetization results. No magnetic scattering from  $Y_2Mo_2O_7$  was observed at low temperature, which is believed to be a result of the small moment on  $Mo^{4+}$ . For  $Tb_2Mo_2O_7$  strong diffuse scattering from the large  $Tb^{3+}$  moments is observed below 25 K. Fourier analysis of this data yields an approximation to the radial correlation function, which gives information concerning spin-spin correlations for the first four coordination shells. The first-, third-, and fourth-neighbor correlations are ferromagnetic, but the second-neighbor correlation is strongly antiferromagnetic. SANS data show magnetic scattering only at large Q, reenforcing the view that antiferromagnetic interactions dominate. The Qintegrated magnetic SANS shows a temperature dependence similar to that for the correlation functions. The long-range order in  $Nd_2Mo_2O_7$  and lack of long-range order in  $Y_2Mo_2O_7$  and  $Tb_2Mo_2O_7$ can be understood, to a certain extent, in terms of Landau-theory results for this highly frustrated lattice.

### I. INTRODUCTION

Pyrochlore oxides have the chemical composition  $A_2B_2O_7$  and crystallize in the cubic, face-centered space group  $Fd\overline{3}m$ , where the *A* and *B* atoms are metals located on the sites 16*d* and 16*c*, respectively, and the oxygens occupy the 48*f* and 8*a* sites. Each of the metal atoms in this system forms an infinite three-dimensional (3D) lattice of corner-sharing tetrahedra. If either the *A* or *B* atom is magnetic, then there is a very high degree of frustration when the nearest-neighbor interactions are antiferromagnetic. A schematic diagram of the tetrahedra formed by the 16*c* lattice within a unit cell is shown in Fig. 1. The 16*d* sublattice is identical to this except for a spatial displacement of  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

The series of pyrochlore oxides  $R_2$  Mo<sub>2</sub>O<sub>7</sub>, R = Nd-Yb, including Y, shows a variety of interesting electrical and magnetic properties that have been reported  $1^{-10}$  recently by several laboratories. The compounds can be divided into two subsets. For R = Nd, Sm, and Gd, metallic and ferromagnetic behavior is found with  $T_c$  values showing a systematic decrease from 93 K (Nd) to 56 K (Gd) across the rare-earth series. For R = Nd and Sm, a second transition is observed at lower temperatures where the net magnetization vanishes. $^{6,10}$  These two compounds also exhibit strong sample history dependence in the low-field magnetization below  $T_c$ . The second subset, R = Tb - Yb, including Y, are semiconductors.  $Y_2Mo_2O_7$  and the solid solutions  $(Y_{1-x}La_x)_2Mo_2O_7$  show spin-glass-like behavior below 20 K in the form of a cusp and sample history dependence in the magnetic susceptibility.<sup>5,7</sup> This result is particularly interesting in the case where x=0 for which there is no evidence for any chemical disorder.<sup>9</sup> The high degree of frustration on the  $Mo^{4+}$  sublattice is

believed to be responsible for these effects. Little is known about the other members of this set. Of particular interest is  $Tb_2Mo_2O_7$  which is positioned at the metal-semiconductor boundary. Evidence for a magnetic transition near 25 K has been reported recently from dc susceptibility measurements.<sup>10</sup>

The related series of compounds  $R_2Mn_2O_7$ (R=Dy-Lu, Y) appear to be ferromagnetic from highfield susceptibility measurements, <sup>11</sup> however, the possibility of nearest-neighbor antiferromagnetic transitions are still discussed by the authors. In fact, further investigations on Y<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub> (Ref. 12) with low-field susceptibility and neutron diffraction show unambiguously that the



FIG. 1. The three-dimensional network of corner-sharing tetrahedra formed by the  $Mo^{4+}$  sublattice in  $R_2Mo_2O_7$  pyrochlores. An outline of the cubic unit cell is also shown.

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nearest-neighbor coupling is antiferromagnetic and higher-neighbor ferromagnetic interactions are responsible for the apparent ferromagnetic behavior in the highfield susceptibility. This material shows spin-glass-like behavior similar to that previously observed in  $Y_2Mo_2O_7$ .

Heat-capacity measurements for the series of compounds  $R_2 Ti_2 O_7$ ,  $R_2 Sn_2 O_7$ , and  $R_2 Zr_2 O_7$  (R=rare earth)<sup>12</sup> show heat-capacity anomalies associated with long-range order in only a few cases, and then only at temperatures below 2 K. The remaining systems show broad features in the heat capacity which may be due to the onset of short-range order over a wide temperature range. This is indirect evidence that the rare-earth exchange coupling in the  $R_2 Mo_2 O_7$  series is relatively weak.

A more complete review of the magnetic properties of oxide pyrochlores can be found in Ref. 13. For a detailed discussion of magnetic ordering in pyrochlores as predicted by mean-field theory, see Ref. 14.

In order to understand the nature of the long- and short-range correlations in a selected subset of this series of compounds we have investigated  $Nd_2Mo_2O_7$ ,  $Tb_2Mo_2O_7$ , and  $Y_2Mo_2O_7$  with small-angle and wide-angle neutron-diffraction techniques. A preliminary report on  $Tb_2Mo_2O_7$  has appeared.<sup>15</sup>

## **II. EXPERIMENTAL DETAILS**

All measurements were performed on the same polycrystalline samples used in Refs. 5-9. Sample preparations are described in Ref. 6.

Wide-angle neutron-diffraction data were obtained at the McMaster Nuclear Reactor (MNR) with 1.3913-Å neutrons. Data sets at 150, 105, 53, and 9 K for Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, at 200, 150, 50, 30, 24, 20, 16, 12, and 8 K for Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> and at 150, 24, and 9 K for Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> were collected. The detector was a three-tube positionsensitive detector (PSD) which has been described previously.<sup>9,16</sup> The sample was held in an aluminum can along with helium exchange gas and sealed with an indium gasket. Small-angle-neutron-scattering (SANS) data were also collected at MNR with 4.75-Å neutrons from a pyrolytic graphite (PG) monochromator. The detector was a  $128 \times 128$ -element 2D PSD providing useful data in the range 0.016 Å<sup>-1</sup>  $\leq Q \leq 0.2$  Å<sup>-1</sup>. Data sets at 300, 50, 30, 25, 20, 16, 12, and 8 K for Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> and at 200, 160, 100, 95, 80, 50, 17, 15, 12 and 10 K for Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> were collected.

Magnetic susceptibility data were collected on a Quantum Design SQUID magnetometer using a pressed polycrystalline pellet. The magnetomer was calibrated with high-purity palladium.

# **III. RESULTS AND DISCUSSION**

#### A. Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

Figure 2 shows the low-temperature data sets with the 150-K data subtracted in order to remove nuclear Bragg scattering and paramagnetic scattering. Small changes in the cell constants with temperature made it necessary to rescale Q space for the 200-K data set at each temperature in such a way that the nuclear reflections would superimpose. This procedure is, of course, only valid for cubic systems. The 53- and 11-K data sets clearly show a Bragg peak near Q=1 Å<sup>-1</sup> which can be indexed as a (111) reflection. Weaker resolution-limited scattering is also observed at the (113) and (331) Bragg angles. The absence of reflections with even (hkl) suggests a magnetic structure that is anti-body-centered. However, this is only possible if the Mo moments are exactly equal and opposite to the Nd moments, which would be accidental, thus the anti-body-centering is most likely only a pseudosymmetry. A number of models consistent with the pseudosymmetry are shown schematically in Fig. 3. Using the atom positions and spin vectors defined in Table I (neglecting face centering, which has no effect on the relative intensities of allowed reflections), we can write down the following expression for the magnetic structure factor:

$$\mathbf{F}_{hkl} = \mu_{Mo} f_{Mo}(Q) [\hat{S}_{1}^{\perp}(1 + \alpha e^{i\pi(k+l)/2}) + \hat{S}_{3}^{\perp}(e^{i\pi(l+h)/2} + \alpha e^{i\pi(h+k)/2})] + \mu_{Nd} f_{Nd}(Q) \cos[\pi(h+k+l)] [\hat{S}_{5}^{\perp}(1 + \alpha e^{i\pi(k+l)/2}) + \hat{S}_{7}^{\perp}(e^{i\pi(l+h)/2} + \alpha e^{i\pi(h+k)/2})], \qquad (1)$$

where  $\mu$  is a magnetic moment in units of  $\mu_B$ , f(Q) is a normalized form factor,  $Q = 4\pi \sin\theta/\lambda$  is the neutronscattering vector,  $\hat{S}_i^{\perp} = \hat{S}_i - \hat{Q}(\hat{S}_i \cdot \hat{Q}), \hat{S}_i$  is a unit spin at site *i*,  $\alpha = \pm 1$  is defined in Table I.

The magnetic form factor for  $Nd^{3+}$  was taken from calculations of Stassis *et al.*<sup>17</sup> and Wilkinson's<sup>18</sup> measured form factor for  $Mo^{3+}$  was used as an approximation for the  $Mo^{4+}$  form factor. The magnetic scattering intensity for powders is now

$$I_{hkl} = (\frac{1}{2}r_0\gamma_0)^2 |\mathbf{4F}_{hkl}|^2 \frac{1}{\sin\theta\sin2\theta} , \qquad (2)$$

where  $\frac{1}{2}r_0\gamma_0=0.27$  is the scattering length per Bohr magneton,  $\theta$  is the scattering angle, and the factor 4 arises because the structure factor only includes  $\frac{1}{4}$  of the unit cell.

Models 1-3 were tested using the Rietveld profile refinement method with the above magnetic cross section. Results are listed in Table II. Figure 4 shows the profile fit for model 1 at 9 and 53 K which is representative of the other fits. Because of the small amount of information contained in the data, all models gave essentially the same  $\chi^2$  for the least-squares fit. A very weak Bragg peak can be seen at the (200) position in the 9-K data set, which is purely magnetic and was obscured in



FIG. 2. Low-temperature wide-angle neutron-diffraction data for  $Nd_2Mo_2O_7$  after subtracting the 150-K data.

the difference plots. For models 2 and 3 both Mo and Nd sublattices have no net moment which is not consistent with the spontaneous moment observed in the magnetization data between 20 and 90 K.<sup>6</sup> Thus, model 1, which is a canted ferrimagnet, is most likely correct at 53 K in spite of the fact that the predicted net moment is very small. On the other hand, at 9 K the magnetization data<sup>6</sup> show a decreasing net magnetization which suggests the onset of one of the antiferromagnetic models (2 or 3). It



FIG. 3. Schematic representations of the three magnetic structural models tested for  $Nd_2Mo_2O_7$ .  $\alpha$  is defined in Table I.

TABLE I. Metal-atom positions and spin vectors in Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>. FC stands for the face-centering operator (0,0,0;  $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0$ ).

Spin number	Species	Fract. coord.	
$\hat{S}_1$	Мо	(0,0,0) + FC	
$\hat{S}_2 = \alpha \hat{S}_1$	Мо	$(0, \frac{1}{4}, \frac{1}{4}) + FC$	
$\boldsymbol{\hat{S}}_3$	Mo	$(\frac{1}{4}, 0, \frac{1}{4}) + FC$	
$\hat{S}_4 = \alpha \hat{S}_3$	Mo	$(\frac{1}{4}, \frac{1}{4}, 0) + FC$	
$\widehat{S}_{5}$	Nd	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + FC$	
$\hat{S}_6 = \alpha \hat{S}_5$	Nd	$(\frac{1}{2}, \frac{1}{4}, \frac{1}{4}) + FC$	
$\widehat{S}_7$	Nd	$(\frac{1}{4}, \frac{1}{2}, \frac{1}{4}) + FC$	
$\hat{S}_8 = \alpha \hat{S}_7$	Nd	$(\frac{1}{4},\frac{1}{4},\frac{1}{2})+\mathbf{FC}$	

is worth mentioning that restricted versions of model 1 with  $\theta_1 = 0$  or  $\theta_2 = 0$  at 53 K were tested giving  $\chi^2$  values near 3.7 and net moments of  $0.34\mu_B$  per half formula unit from the Nd moments.

The low-temperature SANS data for Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> with the 200-K data subtracted are shown in Fig. 5. Magnetic scattering at low Q can be seen at 100, 95, and 80 K. This can be understood in terms of critical scattering from the (000) reflection. Figure 6 shows the Q integrated scattering from 0.04 Å<sup>-1</sup>  $\leq Q \leq 0.15$  Å<sup>-1</sup>. The maximum at 95 K is in accord with the  $T_c$  observed in the magnetization data.<sup>6</sup> The lack of scattering at 50 K



FIG. 4. Observed (+), calculated (-), and difference profiles of the Rietveld fit to the wide-angle neutron data for  $Nd_2Mo_2O_7$  at 9 (top) and 53 K (bottom). Bragg angles are indicated by the vertical bars.

Model	$\chi^2$	$\mu_{ m Mo}$	$\mu_{ m Nd}$	$\mu_{ ext{net}}$	$\theta_1$	$\theta_2$		
9 K								
1	2.5	2.07(11)	0.88(4)	0.80(12)	64(7)	83(10)		
2	2.5	2.14(11)	0.88(2)	0	30(4)	4(6)		
3	2.5	1.90(7)	0.96(8)	0	67(6)	101(11)		
53 K								
1	3.3	1.10(5)	0.95(4)	0.03(6)	41(15)	32(9)		
2	3.3	1.70(3)	0.79(2)	0	62(4)	3(4)		
3	3.5	1.41(3)	0.71(3)	0	44(3)	43(3)		

TABLE II. Magnetic structural parameters obtained from Rietveld analysis.  $\mu_{net}$  are per half formula unit

be interpreted as a lack of scattering at (000) (and thus lack of net magnetization) but merely reflects the fact that the system is long-range ordered with virtually no critical scattering.

#### B. Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

The subtracted 9-K and 24-K data sets are shown in Fig. 7. No obvious signs of diffuse magnetic scattering are visible in the background for each data set. However, resolution-limited peaks are present at the (113) and (331) Bragg angles. The intensity of these peaks are on the order of 5-10% of the unsubtracted nuclear peaks and increase with decreasing temperature. The relative intensities are in accord with the relative intensities of the original nuclear peaks. Also, there is no possible magnetic structure that is consistent with the absence of the (111), (200), and (220) reflections simultaneously (see the Ap-



FIG. 5. SANS data for  $Nd_2Mo_2O_7$  with the 200-K data subtracted.

pendix for details). Thus, we conclude that the origin of the peaks is purely nuclear and could possibly be explained in terms of changes in thermal vibration with temperature. The lack of evidence for long-range order is consistent with the previous results indicating the presence of a spin-glass phase. Any diffuse scattering that may be present due to short-range ordering of the Mo moments will probably be unobservable due to the small  $Mo^{4+}$  moment. This null result for Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> will, however, be quite useful in interpreting the diffuse scattering results for Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> discussed next.

# C. Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

The structure of Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> was refined from neutron powder-diffraction data at room temperature using the Rietveld profile method. The results are consistent with the ideal pyrochlore structure, space group  $Fd\overline{3}m$ ,  $a_0 = 10.309(1)$  Å, with Tb<sup>3+</sup> at the 16*d* sites, Mo<sup>4+</sup> at 16*c*, O<sup>2-</sup> at 8*b*, and 48*f* with x=0.3363(2). There was no evidence for cation disorder. Derived interatomic distances (Mo-O), 2.028 Å and (Tb-O) 2.232(1) Å, 2.484(1) Å are consistent with those found for Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>.<sup>9</sup>

The dc magnetization data (applied field = 2 mT) is



FIG. 6. *Q*-integrated (0.04  $\text{\AA}^{-1} \leq Q \leq 0.15 \text{\AA}^{-1}$ ) magnetic SANS for Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>.



FIG. 7. Low-temperature wide-angle neutron-diffraction data for  $Y_2Mo_2O_7$  after subtracting the 150-K data.

shown in Fig. 8, the behavior is similar in many respects to that normally found for spin glasses. The dc magnetization is independent of sample cooling history above 25 K. Below this temperature the magnetization becomes history dependent, displaying a cusp or weak maximum for the zero-field-cooled data and diverging for the field-cooled case. This is consistent with the magnetization results from Ref. 10. However, the data in Ref. 10 were measured at a slightly higher applied field (0.01 T) and no maximum was observed. Thus, small fields are sufficient to destroy the antiferromagnetism in the material.

Wide-angle neutron scattering data sets for various temperatures are shown in Fig. 9. As before, the high-temperature data (273 K) have been subtracted. Below 30 K broad features appear near Q=1 and 2 Å<sup>-1</sup> with a half-width ten times larger than the resolution half-width. As the temperature was lowered the intensity of the feature increased, whereas the half-width remained



FIG. 8. Magnetic moments vs temperature for  $Tb_2Mo_2O_7$  at an applied field of 2 mT:  $\odot$ , zero field cooled; +, cooled in 0.1 T.

constant.. The resolution-limited scattering near Q=2.1and 2.7 Å<sup>-1</sup> is again believed to be purely nuclear in origin for the reasons described above. It is interesting to note that the peak disappears at the spin-freezing temperature 25 K. The small features at 50 and 150 K are due to slight changes in peak position.

Better insight into the short-range correlations can be obtained by Fourier transforming the data, which gives the radial correlation function<sup>19</sup>

$$g(r) = \int_{Q_l}^{Q_h} I_{\text{diff}}(Q) f(Q)^{-2} Q \sin(Qr) dQ , \qquad (3)$$

where  $I_{\text{diff}}(Q)$  is the magnetic scattering intensity at Q with the paramagnetic scattering subtracted and f(Q) is magnetic form factor. In the limit of isotropic interactions,

$$g(\mathbf{r}) = \frac{1}{S(S+1)} \sum_{\mathbf{r}'} \langle \mathbf{S}_0 \cdot \mathbf{S}_{\mathbf{r}'} \rangle \delta(|\mathbf{r}| - |\mathbf{r}'|) , \qquad (4)$$

which is a sum of spin-spin correlations at distance r. The major limitation in this sort of analysis is most likely from the limited Q range of the data. Other sources of error such as data noise and anisotropy are less significant.

The Fourier-transformed data are shown in Fig. 10 with first to fourth-neighbor bond distances indicated. Only the second-neighbor correlations are net antiferromagnetic. An abrupt change in the qualitative features of the correlation function occurs between 24 and 30 K which is in accord with the onset of spin-glass-like behavior at 25 K from the magnetization results.



FIG. 9. Low-temperature wide-angle neutron-diffraction data for  $Tb_2Mo_2O_7$  after subtracting the 300-K data.



FIG. 10. Real-space radial correlation function (in arbitrary units) obtained by Fourier transforming the  $Tb_2Mo_2O_7$  wideangle data collected at various temperatures. Arrows indicate the four nearest coordination shell distances for the metal atoms.

the subtracted data with a cross section first described by Bertaut and Burlet<sup>19,20</sup> for scattering due to short-range spin-spin correlations in spin glasses, applied here to the pyrochlore system:

$$I(Q) = N[\frac{1}{2}r_0\gamma_0 f_m(Q)]^2 \frac{2}{3} \sum_{i=1}^4 c_i \gamma_i \frac{\sin QR_i}{QR_i} , \qquad (5)$$

where

$$\gamma_1 = 2 \langle \mu_{\mathrm{Tb}} \mu_{\mathrm{Mo}} \rangle_{R1} + \langle \mu_{\mathrm{Tb}} \mu_{\mathrm{Tb}} \rangle_{R1} + \langle \mu_{\mathrm{Mo}} \mu_{\mathrm{Mo}} \rangle_{R1} , \qquad (6a)$$

 $\gamma_2 = 2 \langle \mu_{\rm Tb} \mu_{\rm Mo} \rangle_{R2} , \qquad (6b)$ 

$$\gamma_{3} = 2 \langle \mu_{\mathrm{Tb}} \mu_{\mathrm{Mo}} \rangle_{R3} + \langle \mu_{\mathrm{Tb}} \mu_{\mathrm{Tb}} \rangle_{R3} + \langle \mu_{\mathrm{Mo}} \mu_{\mathrm{Mo}} \rangle_{R3} , \qquad (6c)$$

$$\gamma_4 = \langle \mu_{\rm Tb} \mu_{\rm Tb} \rangle_{R4} + \langle \mu_{\rm Mo} \mu_{\rm Mo} \rangle_{R4} . \tag{6d}$$

The summation is over coordination shells from a central atom and the  $R_i$  and  $c_i$  are bond distances and numbers of neighbors known from crystallographic data. Only the sum of correlations at each bond distance can be determined from the data. Of course, one would expect  $\gamma_1, \gamma_3$ , and  $\gamma_4$  to be dominated by Tb-Tb correlations as the Tb moment is about nine times larger than the Mo moment. In fact, the lack of diffuse scattering for  $Y_2Mo_2O_7$  indicates that  $\langle \mu_{Mo} \mu_{Mo} \rangle$  correlations can be neglected in this analysis. It is for this reason that the difference between the magnetic form factors for Tb<sup>3+</sup> and Mo<sup>4+</sup> was ignored in cross section. Figure 11 (top) shows the temperature dependence of the four  $\gamma$  values determined by fitting the subtracted data with the above cross section. The absolute values of the  $\gamma_i$  increase sharply below about 25 K. Only  $\gamma_2$ , corresponding to the Tb-Mo coupling, is negative.

SANS data difference plots (Fig. 12) show enhanced scattering only for Q > 0.04 Å<sup>-1</sup>. The temperature dependence of this excess SANS (Fig. 11, bottom) closely follows that of the correlation coefficients. The fact that the magnetic SANS occurs only for high Q provides rein-



FIG. 11. Top: temperature dependence of the correlation coefficients (see text) obtained by profile fitting the subtracted data for  $Tb_2Mo_2O_7$  at each temperature. Bottom: temperature dependence of the *Q*-integrated magnetic SANS data.

forcement of the conclusion, drawn from the analysis of the diffuse scattering, that antiferromagnetic exchange predominates in this material.

# **IV. COMPARISON WITH LANDAU THEORY**

Full details of the Landau theory for pyrochlores have been presented elsewhere.<sup>14</sup> Some results that are



FIG. 12. SANS data for  $Tb_2Mo_2O_7$  with the 300-K data subtracted.

relevant to  $R_2 Mo_2 O_7$  pyrochlores will be discussed here. In order to simplify the calculations somewhat, the structure will be described in a nonstandard rhombohedral setting with a unit cell having one-quarter the volume of the cubic cell. The lattice vectors of the two systems are related by

$$\begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}^{\text{rhom}} = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}^{\text{cubic}} .$$
(7)

The advantage of the rhombohedral basis is that there are only 4 Mo<sup>4+</sup> and  $R^{3+}$  atoms per unit cell as opposed to 16 of each per cell in the cubic system. The corresponding space group is  $R\bar{3}m$ , which is a subgroup of  $Fd\bar{3}m$ . Thus, the rhombohedral representation has the disadvantage that some of the inherent symmetry is hidden. Table III shows a list of Mo<sup>4+</sup> and  $R^{3+}$  atom positions for both systems along with their nearest neighbors (NN's) listed by atom number. The factor of 2 in front of each list of NN's indicates that there are two of each type of NN which is related by spatial inversion. Following the notation in Ref. 14, we can write down the Landau free energy as follows:

$$F(T) = -\frac{1}{2} \sum_{ij} \sum_{ab} J_{ij}^{ab} \mathbf{B}_{i}^{a} \cdot \mathbf{B}_{j}^{b} + \frac{nT}{2} \sum_{i,a} (B_{i}^{a})^{2} + O(B^{4}) , \quad (8)$$

where summations are over all unit cells (ij) and atoms within the unit cell (ab),  $\mathbf{B}_i^a = \langle \mathbf{S}_i^a \rangle$  are the thermal expectation values of the *n*-component unit spins, and the *J*'s are exchange interactions. The first two terms in (8) are, respectively, the internal energy and the lowest-order entropy contribution. Entropy terms of order  $B^4$  and higher will not be considered here as we are only concerned with nature of the highest-temperature ordered phase. After Fourier transforming (8), we have the free energy per unit cell

$$f(T) = \frac{1}{2} \sum_{\mathbf{q}} \sum_{ab} \mathbf{B}_{\mathbf{q}}^{a} \cdot \mathbf{B}_{-\mathbf{q}}^{b}(nT\delta^{ab} - J_{\mathbf{q}}^{ab}) + O(B^{4}) , \qquad (9)$$

where

$$J_{\mathbf{q}}^{ab} = \sum_{ij} J_{ij}^{ab} \exp[i\mathbf{q} \cdot (\mathbf{R}_i^a - \mathbf{R}_j^b)], \qquad (10)$$

 $\mathbf{R}_i^a$  is an atom position,  $\mathbf{q}$  is a wave vector in the first Brillouin zone, and  $\delta^{ab}$  is a Kronecker  $\delta$ . Because we are dealing with a non-Bravias lattice, Fourier transforming is not sufficient to diagonalize the second-order term which dominates the free energy for small *B*. Transforming to normal modes ( $\phi$ ) of the system, we have

$$f(T) = \frac{1}{2} \sum_{\mathbf{q},i} |\phi_{\mathbf{q}}|^2 (nT - \lambda_{\mathbf{q}}^i) + O(\phi^4) , \qquad (11)$$

where  $\lambda_{q}^{i}$  are eigenvalues of  $J_{q}^{ab}$ . The first ordered state of the system will occur at a temperature

$$T_c = \frac{1}{n} \max\{\lambda_q^i\} , \qquad (12)$$

where max{} indicates a global maximum for all *i* and **q**. Usually there will be a small number of symmetry-related **q** vectors characterizing the ordered state. The modes corresponding to max{ $\lambda_{q}^{i}$ } are sometimes referred to as critical modes or unstable modes (unstable because the corresponding **q**-dependent susceptibility  $\chi_{q}$  diverges at  $T_{c}$ ) of the system.

From (10) and the information in Table III, one can calculate the  $8 \times 8$  matrix  $J_q^{ab}$  for the general pyrochlore problem with nearest-neighbor interactions. We first define

Atom		F	osition	
Site	No.	Rhom	Cubic	Nearest neighbors
16 <i>c</i>	Mo1	(0,0,0)	(0,0,0) + FC	$2 \times Mo(2,3,4), \ 2 \times R(2,3,4)$
16c	Mo2	$(\frac{1}{2}, 0, 0)$	$(0, \frac{1}{4}, \frac{1}{4}) + FC$	$2 \times Mo(1,3,4), 2 \prec R(1,3,4)$
16 <i>c</i>	Mo3	$(0, \frac{1}{2}, 0)$	$(\frac{1}{4}, 0, \frac{1}{4}) + FC$	$2 \times Mo(1,2,4), 2 \times R(1,2,4)$
16 <i>c</i>	Mo4	$(0,0,\frac{1}{2})$	$(\frac{1}{4},\frac{1}{4},0)+FC$	$2 \times Mo(1,2,3), 2 \times R(1,2,3)$
16 <i>d</i>	<i>R</i> 1	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + FC$	$2 \times Mo(2,3,4), 2 \times R(2,3,4)$
16 <i>d</i>	<i>R</i> 2	$(0,\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2}, \frac{1}{4}, \frac{1}{4}) + FC$	$2 \times Mo(1,3,4), \ 2 \times R(1,3,4)$
16 <i>d</i>	<i>R</i> 3	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{4}, \frac{1}{2}, \frac{1}{4}) + FC$	$2 \times Mo(1,2,4), 2 \times R(1,2,4)$
16 <i>d</i>	<i>R</i> 4	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{2}) + FC$	$2 \times Mo(1,2,3), 2 \times R(1,2,3)$

TABLE III. Pyrochlore metal-atom positions in rhombohedral and cubic basis. Nearest neighbors are listed by atom number. FC stands for the face-centering operation  $(0,0,0; 0,\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},0)$ .

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$$\mathcal{A}_{intra} = 2 \begin{bmatrix} 0 & \cos(q_x) & \cos(q_y) & \cos(q_z) \\ \cos(q_x) & 0 & \cos(q_x - q_y) & \cos(q_z - q_x) \\ \cos(q_y) & \cos(q_x - q_y) & 0 & \cos(q_y - q_z) \\ \cos(q_z) & \cos(q_z - q_x) & \cos(q_y - q_z) & 0 \end{bmatrix},$$

which are, respectively, the intrasublattice and the intersublattice coupling matrices for the Mo (16c) and the R(16d) sites. The full coupling matrix now has the form

$$J_{\mathbf{q}}^{ab} = \begin{bmatrix} J_1 & \mathcal{J}_{\text{intra}} & J_{12} & \mathcal{J}_{\text{inter}} \\ J_{12} & \mathcal{J}_{\text{inter}} & J_2 & \mathcal{J}_{\text{intra}} \end{bmatrix},$$
(14)

where  $J_1$  and  $J_2$  are couplings for metal atoms within the 16c and 16d sublattices, respectively, i.e., the Mo-Mo and R-R couplings, and  $J_{12}$  is the coupling between 16c and 16d or the Mo-R coupling.

In this problem we are dealing with a threedimensional coupling parameter space spanned by  $J_1$ ,  $J_2$ , and  $J_{12}$ . The effects of further neighbor interactions will not be considered here. In general, the magnetic species on the two sublattices will have different moments which can be absorbed into the J's in such a way that all spins are still unit vectors. Figures 13(a) and 13(b) show maps of the ordering wave vectors in the parameter space of  $J_2$ and  $J_{12}$  for  $J_1=0$  and -1, respectively, which covers all cases of interest. The phase diagram is seen to be invariant under changes in the sign of  $J_{12}$ .

The large regions where the q=0 mode becomes ordered below  $T_c$  would correspond to the situation in Nd<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>. The Landau theory for this model with the fourth-order term is rather involved and will not be discussed here except to say that two  $T_c$ 's and complex behavior in the magnetization curve are predicted.

The dotted lines along  $J_{12}=0$  in both diagrams indicate regions where the whole zone is degenerate. In this case, which is relevant to  $Y_2Mo_2O_7$ , one only need consider  $\mathcal{J}_{intra}$  which can be diagonalized explicitly for general **q** and has the following eigenvalues:

$$\begin{split} \lambda_{q}^{1} &= \lambda_{q}^{2} = -2J_{1} , \\ \lambda_{q}^{3} &= 2J_{1}(1 - \sqrt{1 + Q}) , \\ \lambda_{q}^{4} &= 2J_{1}(1 + \sqrt{1 + Q}) , \\ Q &= \frac{1}{2} [\cos(2q_{x}) + \cos(2q_{y}) + \cos(2q_{z}) \\ &+ \cos(2q_{x} - 2q_{y}) + \cos(2q_{y} - 2q_{z}) \\ &+ \cos(2q_{z} - 2q_{x})] . \end{split}$$
(15)

Note that  $\lambda^1$  and  $\lambda^2$  are completely independent of **q** and that these are the maximal eigenvalues for the system

when  $J_1 < 0$ , which is the relevant case. Dispersion curves for the four modes are shown in Fig. 14, from which one can see that mode 3 is also degenerate with 1 and 2 at q=0. Thus, mean-field theory predicts a special temperature  $T_c = \frac{2}{3}|J_1|$  below which the system preferen-



FIG. 13. Ordering wave vectors in the coupling parameter space  $J_2$  and  $J_{12}$  with  $J_1=0$  in (a) and  $J_1=-1$  in (b) for two sublattice pyrochlores with NN interactions. Along the dashed line the system is continuously degenerate and critical throughout the whole zone. "No Disp." indicates that the system is continuously degenerate along the (0,q,q) directions.

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(13)



FIG. 14. Dispersion curves along certain symmetry directions for one sublattice pyrochlore systems with only NN exchange interactions. The unstable or critical modes will have the largest eigenvalue  $\lambda_q$  which is measured in units of  $J_1$ , the NN coupling constant.

tially samples modes 1 and 2, i.e., a phase space with half the dimensionality. Because the system can sample a macroscopic number of Fourier modes below  $T_c$ , no long-range order is predicted within the mean-field approximation. One can understand this unusually high degree of degeneracy in terms of the strongly frustrated nature of antiferromagnetic ordering on a tetrahedron. The fact that the tetrahedra forming the Mo<sup>4+</sup> sublattice are rather sparely connected (corner sharing as can be seen from Fig. 1) will also inhibit long-range order. Of course, weaker forces such as further-neighbor interactions or dipole forces will lift some of this degeneracy, but these forces will not be effective unless  $T \ll J_1$ .

Of particular interest is the large region in Fig. 13(b) where the system is continuously degenerate along the (0,q,q), direction. This situation is similar to that for  $Y_2Mo_2O_7$  with the additional presence of  $J_2$  and  $J_{12}$  interactions which lift some, but not all, of the degeneracy. Again one expects no long-range order for such model systems. The couplings in Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> are most likely in the dispersionless or the incommensurate region on the  $J_{12} < 0$  side of the diagram. Although long-range order is predicted for the incommensurate models,  $T_c$  will be greatly depressed by thermal fluctuations since the maxima in  $\lambda_q$  are very weak.

#### V. SUMMARY AND CONCLUSIONS

Both  $Y_2Mo_2O_7$  and  $Tb_2Mo_2O_7$  are spin-glass-like in the absence of chemical disorder which is indeed unusual. This can be partially understood in terms of the highly frustrated nature of the antiferromagnetically coupled Mo sublattice. In the absence of further-neighbor interactions, such a system is not expected to order at any temperature.<sup>21,22</sup> Villain calls these systems cooperative paramagnets.<sup>22</sup> The Landau-theory result explains this phenomenon in terms of a macroscopic degeneracy of the Fourier modes for all **q** vectors in the zone. Below a temperature on the order of the nearest-neighbor exchange constant  $J_1$ , the system will preferentially sample half of the phase space and short-range correlations will develop. These correlations are almost certainly present in  $Y_2Mo_2O_7$ , however, the small Mo moment does not allow us to see any diffuse neutron scattering (which is generally fairly weak even for systems with larger moments) in the background. For  $Tb_2Mo_2O_7$  one can expect more than an order magnitude more scattering intensity overall, and the effects of the short-range order on the neutron-scattering background are quite dramatic. This indicates that the nearest-neighbor Tb-Tb coupling is weakly ferromagnetic and that Tb-Mo coupling is antiferromagnetic. Scattering from Mo-Mo correlations is most likely not observable in light of the  $Y_2Mo_2O_7$  results.

 $Nd_2Mo_2O_7$  is one of the rare instances of long-range magnetic order in pyrochlore oxides. Due to the high symmetry of the metal sublattices, the magnetic structure cannot be determined unambiguously from powder data. A canted ferrimagnetic model and two antiferromagnetic models all gave equally good fits at 9 and 53 K. In an effort to be consistent with magnetization data<sup>6</sup> we believe that the ferrimagnetic structure exists from 95 to about 20 K. Below 20 K antiferromagnetic ordering occurs which is highly frustrated and the magnetization data show strong sample history dependence similar to that observed for Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>.<sup>5</sup>

Neutron-diffraction experiments on Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> at temperatures below 1 K and on field-cooled samples would probably show some very interesting results. Other compounds in the series with small neutron absorption cross sections (such as Ho<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>) should also be investigated. More detailed theoretical work is also of paramount importance. In particular, the effects of thermal fluctuations may select certain Fourier modes thus giving long-range order. This would most easily be tested with Monte Carlo simulations. The problem of whether or not quantum spins can order on this interesting lattice is currently under investigation.<sup>23</sup> This is most relevant to  $Mo^{4+}$  where S=1. It is generally believed that, in order to observe spin-glass behavior, there must be some sort of disorder in the compound. This does not seem to be the case in pyrochlore antiferromagnets. Further investigation of pyrochlore systems may give some insight into the role that frustration plays in the spinglass problem.

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### APPENDIX

In order to prove that the simultaneous absence of the (111), (200), and (220) magnetic reflections in  $Y_2Mo_2O_7$  is inconsistent with any non-zero-ordered moment, we first write down the Mo<sup>4+</sup> contribution to the magnetic structure factor (1)

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(A1)

$$\mathbf{F}_{hkl} \propto \mathbf{S}_1^{\perp} + \mathbf{S}_2^{\perp} e^{i\pi(k+l)/2} + \mathbf{S}_3^{\perp} e^{i\pi(h+l)/2} + \mathbf{S}_4^{\perp} e^{i\pi(h+k)/2}$$

where

$$S_x^{\perp} = S_x - h \frac{hS_x + kS_y + lS_z}{h^2 + k^2 + l^2}$$
, (A2)

and similarly for y and z. In order for the (111) powder reflection to be absent, we must have F(111)=0,  $F(1\overline{1}\overline{1})=0$ ,  $F(\overline{1}\overline{1}\overline{1})=0$ , and  $F(\overline{1}\overline{1}1)=0$ . Solving these four equations gives the following set of conditions on the spin vectors:

$$S_{1x} = -S_{2y} = -S_{3z} , \qquad (A3a)$$

$$S_{2x} = -S_{1y} = -S_{4z}$$
, (A3b)

$$S_{3x} = -S_{4y} = -S_{1z}$$
, (A3c)

$$S_{4x} = -S_{3y} = -S_{2z} \ . \tag{A3d}$$

Similarly, the absence of the (200) and (220) reflections gives

and  $S_{2x} = S_{3x}$  ,

 $S_{1x} = S_{4x}$ 

$$S_{1y} = S_{3y}$$
  
and

$$S_{2y} = S_{4y}$$
,

 $S_{3z} = S_{4z}$  ,

 $S_{1z} = S_{2z}$ 

$$S_1 = S_2 = S_3 = S_4$$
, (A5)

respectively. Conditions (A3)-(A5) can only be simultaneously satisfied if all  $S_i = 0$ , which implies no long-range-ordered moment.

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(A4a)

(A4b)

(A4c)