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BRIEF COMMUNICATION

The Crystal Structure of the Spin-Glass Pyrochlore, $Y_2Mo_2O_7$

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The crystal structure of the spin-glass material, $Y_2Mo_2O_7$, has been determined from powder neutron diffraction data using profile (Rietveld) methods. The data are consistent with the fully ordered cubic pyrochlore structure, $a_0 = 10.230(1)$ Å with Y in 16*d*, Mo in 16*c*, O in 48*f*($x = 0.3382(1)$), and O′ in 8*b* of *Fd3m*. Attempts to refine models with O′ disordered over the 32*e* sites or between the 8*a* and 8*b* sites resulted in convergence to the 8*b* positions. Derived Y–O and Mo–O distances are in excellent agreement with those found in isostructural materials giving indirect evidence for Y–Mo ordering over the cation sites.

Introduction

Recently, it has been shown that $Y_2Mo_2O_7$ and the related $(La_xY_{1-x})_2Mo_2O_7$ phases exhibit magnetic properties similar to those observed in spin-glass materials (*1*, *2*). To date, without exception, such behavior has been restricted to positionally disordered systems such as true glasses, amorphous materials, random alloys, or solid solutions. On the basis of lattice constants near 10 Å and the general appearance of the X-ray powder patterns, $Y_2Mo_2O_7$ and similar materials have been described in terms of the cubic pyrochlore structure (*1–3*). For this structure type and stoichiometry the conventional description involves full occupancy of the 16*d*(Y), 16*c*(Mo), 48*f*(O), and 8*b*(O′) in *Fd3m* (No. 227). The observation of spin-glass behavior in such a well-ordered system would be unprecedented. For this reason, we have undertaken a structure refinement of $Y_2Mo_2O_7$ with particular attention paid to the issue of positional order/disorder.

Due to the favorable scattering power of oxygen for thermal neutrons, the structure was determined from powder neutron diffraction data.

Experimental

Samples were prepared and characterized as described in a previous publication (*1*).

Neutron diffraction data were obtained at

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the McMaster Nuclear Reactor using 1.3935-Å neutrons obtained from a [200] copper monochromator. Data were collected using a position-sensitive detector (PSD) which is essentially the same as that in use at the Missouri University Research Reactor (MURR) which has been described previously (*4*). Soller-type collimators are not currently used but an oscillating–rotating collimator (ORC) is in place between the sample and the PSD to reduce background levels (*4*). The resolution of the above system is similar to that of the facility of MURR but FWHM values for standard materials are about 20–25% greater in the same 2θ range for samples of similar diameter. At the present sample-to-detector distance of 1060 mm and the operating wavelength, useful data are collected over a 25° 2θ range for a single detector setting. Thus, a typical dataset requires collection of four to five such frames.

The raw data are then corrected for the detector geometry and refined according to the procedures of Ref. (*4*). Refinement is carried out with a version of the Rietveld profile refinement program as modified by A. W. Hewat and E. Prince with further modifications added locally by M. Eitel.

The dataset for $Y_2Mo_2O_7$ was collected on a sample of approximately 7 g contained in a thin-walled vanadium can at room temperature.

Results and Discussion

The initial refinement was carried out for the fully ordered model. Following refinement of scale, background, cell constants, zero point, and half-width parameters, the positional and isotropic thermal factors were refined to the values shown in Table I.

Clearly, the fully ordered model provides an excellent fit to the data as indicated by the agreement indices and the appearance of the fitted profile in Fig. 1.

Although there was no evidence that the fully ordered model was inadequate, some disordered models were investigated. Hubert (*3*) has suggested that the O′ atoms normally assigned to the 8*b* sites can be disordered over the 32*e* sites. An attempt to refine such a model resulted in no significant improvement to R_{wp} and the final value of the x parameter, 0.375(3), was not significantly different from $\frac{3}{8}$. Another possibility is the distribution of O′ over the 8*b* and the normally vacant 8*a* sites as has been proposed for some nonstoichiometric lanthanide zirconates (*5*). Refinement of the occupancy factors for the 8*b* and 8*a* sites showed no significant amount of O′ in 8*a*; $n(8a) = 0.03(2)$.

As pointed out by Sleight (*6*), the unusual coordination geometry of the 16*d* site in pyrochlores leads to a large thermal anisotropy. Anisotropic thermal parameters were refined for the Y, 16*d*, site to the following values: $\beta_{11} = \beta_{22} = \beta_{33} = 0.00138(9)$ and $\beta_{12} = \beta_{13} = \beta_{23} = -0.00016(10)$. These values indicate an ellipsoid compressed along the 3 axis as has been noted for other pyrochlores (*6*, *7*). The rms displacement is 0.075(7) Å along the axis and 0.090(7) Å normal to the axis. Refinement of anisotro-

TABLE I

STRUCTURE AND THERMAL PARAMETERS FOR $Y_2Mo_2O_7$, FULLY ORDERED MODEL, 298 K (SPACE GROUP *Fd3m*)

$a_0 = 10.230(1)$ Å

Atom	x	y	z	B (Å^2)
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.63(4)
Mo	0	0	0	1.18(4)
O	0.3382(1)	$\frac{1}{8}$	$\frac{1}{8}$	0.82(3)
O′	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	1.15(9)

$R_N = 0.035$
$R_p = 0.042$ No. observations = 1853
$R_{wp} = 0.060$ No. independent Bragg reflections = 44
$R_E = 0.024$

Note. Definitions of the agreement indices: $R_{wp} = \Sigma w|Y_{obs} - Y_{calc}|^2/\Sigma w|Y_{obs}|^2)^{1/2}$; $w = 1/Y_{obs}$; $R_p = (\Sigma|Y_{obs} - Y_{calc}|^2/\Sigma|Y_{obs}|^2)^{1/2}$; $R_N = \Sigma|I_{obs} - I_{calc}|/I_{obs}$; R_E = (degrees of freedom/$\Sigma w(|Y_o|)^2)^{1/2}$; Degrees of freedom = (number of profile points) − (number of parameters).

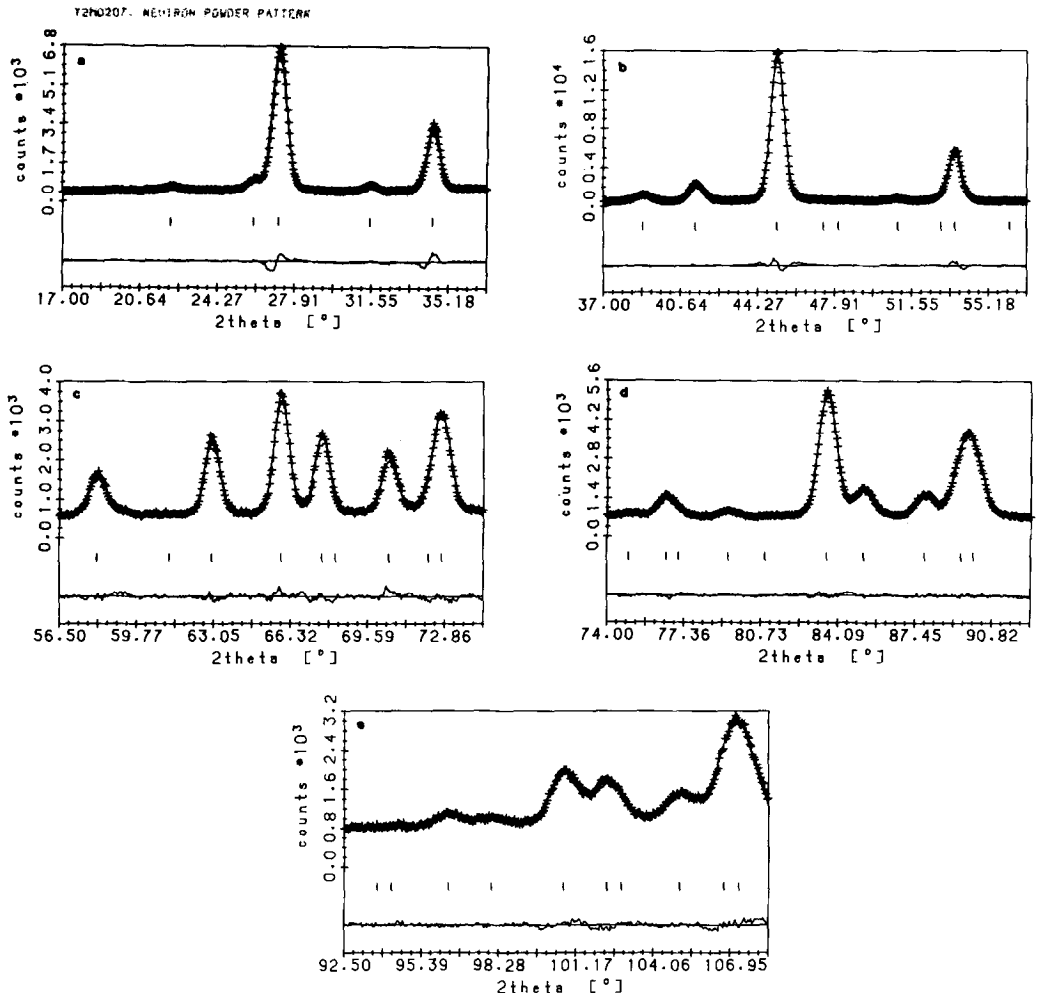

FIG. 1. Neutron powder pattern. The observed (+), calculated (−), and difference profiles for $Y_2Mo_2O_7$. Positions of Bragg reflections are indicated.

pic thermal parameters for Y resulted in $R_{wp} = 0.059$ and $R_N = 0.031$.

Selected bond distances and angles for $Y_2Mo_2O_7$ are shown in Table II.

The values in Table II can be compared with bond distances in similar materials as shown in Table III. It is clear that the observed Y–O and Mo–O distances in $Y_2Mo_2O_7$ are in excellent agreement. This is strong indirect evidence for positional order between Y and Mo. Direct evidence is

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $Y_2Mo_2O_7$

	Y–O (48*f*)	2.4512(7)	
	Y–O (8*b*)	2.2149(2)	
	Mo–O (48*f*)	2.0214(7)	
O–Mo–O	99.50(4)	O–Y–O	115.60(6)
O–Mo–O	80.50(8)	O–Y–O	64.40(6)
Mo–O–Mo	126.93(16)	O–Y–O	102.28(5)
Y–O–Y	95.09(11)	O–Y–O	77.72(5)
Y–O–Y	107.55(3)		

TABLE III

TYPICAL BOND DISTANCES FOR Y–O AND Mo–O IN RELATED OXIDES (*7–11*) IN Å

Mo–O	Y–O (48*f*)	Y–O (8*b*)
2.011 (MoO_2 ave. 6 values)	2.473(21) ($Y_2Ti_2O_7$)	2.1856(6) ($Y_2Ti_2O_7$)
2.029 ($Zn_2Mo_3O_8$ ave. 4 values)	2.485(12) ($Y_2Sn_2O_7$)	2.2457(10) ($Y_2Sn_2O_7$)
	2.447(6) ($Y_2Mn_2O_7$)	2.1429(1) ($Y_2Mn_2O_7$)
Ave. = 2.020	Ave. = 2.468	Ave. = 2.1917

difficult to obtain from the data due to the similar scattering lengths of Y and Mo, 0.775 and 0.695, respectively, for thermal neutrons. It should be noted that significant positional Y–Mo disorder would imply bond distances intermediate to those observed and an x parameter for the 48*f* O atoms close to 0.375, the value expected for a disordered-fluorite model.

Summary and Conclusions

The refined crystal structure of $Y_2Mo_2O_7$ is consistent with the fully ordered cubic pyrochlore model. In view of the spin-glass-like magnetic properties of $Y_2Mo_2O_7$, this situation is, to our knowledge, unprecedented.

A clue to the origin of this apparent paradox may be provided by the calculations of Liebmann (*12*). It has been recognized for some time that the 16*c* sites in *Fd3m* constitute a magnetic sublattice with a high potential degree of frustration (*13, 14*). Liebmann has shown that within the Ising approximation the n.n. AF pyrochlore lattice does not order. No results are known for either the Heisenberg or XY model but it is likely that they will order at finite temperatures. Thus, it is possible that $Y_2Mo_2O_7$ represents such an Ising system and that the spin-glass behavior arises from a degree of disorder which is not detectable within the limitations of a diffraction experiment. Further work is underway to clarify this situation.

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