JOURNAL OF SOLID STATE CHEMISTRY 67, 248–253 (1987)

Pyrochlore Solid Solutions $(La_xY_{1-x})_2Mo_2O_7$, $x = 0.0$ to 0.5. Spin-Glass-like Behavior

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Received April 14, 1986

The $(La_xY_{1-x})_2Mo_2O_7$ system was investigated in the range $x = 0.0$ to $x = 0.5$. Single-phase materials exist up to $x = 0.4$; the $x = 0.5$ composition has a small impurity contamination. The lattice constants are linear with x and range from 10.224 Å ($x = 0.0$) to 10.461 Å ($x = 0.5$). These lattice constants span the same range as the $R_2Mo_2O_7$ series from $R = Y$ to $R = Nd$. In this series, there is a discontinuous change from ferromagnetic long-range order to short-range spin-glass-like order between $R = Gd$ and $R = Tb$. Yet, the solid solutions all show spin-glass-like properties with maxima in the susceptibility in the 20–25 K range and sample-history-dependent effects at lower temperatures. Deviations from the Curie-Weiss Law occur well above the susceptibility maxima. The Weiss constants change from −61 to +41 K for $x = 0.0$ and $x = 0.5$, respectively, indicating a competition between antiferromagnetic and ferromagnetic exchange interactions. This competition, coupled with the inherent frustration of the Mo^{4+} lattice in space group $Fd3m$ is a possible origin of the spin-glass properties.

Introduction

The $R_2M_2O_7$ pyrochlores, where $R \equiv$ rare earth and M is any metallic element with a stable (IV) oxidation state form an extensive series of isostructural materials the structure and properties of which have recently been reviewed (*1*). Although some work on the magnetic properties of these compounds has been reported, many gaps still exist both in knowledge and understanding. For the case of diamagnetic M(IV), e.g., Ti(IV), magnetic order occurs only at very low temperatures near 1 K (R = Dy, Ho, Er) and well below, $T_c = 0.2$ K (R = Yb) (*2*), but the magnetic structures are unknown. Anomalies in the specific heat are found at temperatures well above the reported T_c's (*2*). When M is a transition element reports of magnetic order are also rare. Among the 3*d* group elements, M = V, Cr, and Mn, the $R_2V_2O_7$ (R = Ln, Yb, Tm) order ferromagnetically near 72 K, (*3–5*) while paramagnetic behavior is reported for M = Cr and Mn (*6*). Only the $R_2Mo_2O_7$ phases, among all known pyrochlores containing a 4*d* or 5*d* series element, show magnetic order. Ferromagnetism is reported for R = Nd and Sm while R = Gd might be ferrimagnetic at temperatures in

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0022-4596/87 $3.00

the range 80 to 100 K (*7–9*). The remaining members of the series, R = Tb → Yb do not order to 4.2 K (*9*). Measurement of the Weiss constant indicates that the sign of the net Mo–Mo exchange interaction varies from ferromagnetic, $\theta_c = +115$ K (R = Nd), to antiferromagnetic, $\theta_c = -25$ K (R = Yb) across the lanthanide series (*9*).

The compound $Y_2Mo_2O_7$ with a diamagnetic R ion was found to have remarkable properties. This material shows spin-glass-like behavior below 20 K in spite of the fact that $Y_2Mo_2O_7$ is a concentrated system with no obvious evidence for significant positional disorder on the Mo(IV) magnetic sublattice or indeed on the diamagnetic sublattices (*10*). This issue is currently under investigation. Regardless of its origin, the existence of spin-glass-like behavior in $Y_2Mo_2O_7$ provides a possible clue to the rather discontinuous variation in magnetic properties with R in this series. For example, $Gd_2Mo_2O_7$ is a ferromagnet or ferrimagnet, T_c = 83 K, while $Tb_2Mo_2O_7$ does not order in the long-range sense to 4.2 K and these are adjacent series members (*9*)!

Some assumptions are useful here. First, it is assumed that the Mo(IV)–Mo(IV) exchange interaction is the most important one and, second, that both ferromagnetic and antiferromagnetic interactions are present. Then, there seems to be a crucial magnitude of the ferromagnetic component above which true long range ferromagnetic order occurs (R = Nd, Sm, and Gd) and below which the system is sufficiently frustrated that long-range order is impossible, (R = Tb → Yb, Y). Apparently, this parameter is extraordinarily sensitive to the size and, perhaps, electronic properties of the rare earth. One convenient measure of the relative magnitudes of competing exchange interactions is the Weiss constant, θ_c, which reflects their algebriac sum. For the $R_2Mo_2O_7$ series, previously studied, the R–Mo and R–R interactions as well as crystal field effects will contribute to θ_c. It would be better to work with a series containing only diamagnetic rare earths but retaining some flexibility regarding size variations. The solid solutions $(La_xY_{1-x})_2Mo_2O_7$ represent a reasonable approximation to these goals. Some of their properties are reported in the following.

Experimental

Materials preparation. The samples used in this study were prepared by heating a mixture with an appropriate molar ratio of $(La_{1-x}Y_x)_2O_3$ and MoO_2 in a $CO/CO_2 = 1$ buffer gas atmosphere for 24 to 48 hr at 1400°C.

To obtain a homogeneous mixture of La_2O_3 and Y_2O_3, the $(La_xY_{1-x})_2O_3$ sample was prepared by thermal decomposition of lanthanum–yttrium mixed oxalates precipitated from chloride solution with oxalic acid. Products were analyzed by thermal gravimetric analysis in air and by wet chemical methods. More details of the preparative and analytical methods are given elsewhere (*9*).

Magnetic measurements. Magnetic data were collected in the temperature range 42–300 K with applied field from 0.0045 T (residual field of our electromagnetic) to 1.5 T using a PAR vibrating sample magnetometer calibrated with a high-purity nickel sample. Temperature was measured using a calibrated chromel-gold 0.07% iron thermocouple. Corrections for diamagnetism to the measured susceptibility were applied with the values reported by Selwood (*11*). Diagmagnetic susceptibilities, χ_d, ranged from -142×10^{-6} emu/mole for $Y_2Mo_2O_7$ to -150×10^{-6} emu/mole for $(La_{0.5}Y_{0.5})_2Mo_2O_7$.

Powder X-ray diffraction. X-ray powder data were obtained using monochromatized Cu$K\alpha$ radiation on a Philips diffractometer. Optical grade KCl was added as an internal standard. Unit cell constants were deter-

mined from 10 indexed reflections by least-squares refinement.

Results and Discussion

From X-ray powder diffraction evidence, the solid solution members from $x = 0$ ($Y_2Mo_2O_7$) to $x = 0.4$ could be prepared as single-phase materials. For $x = 0.5$, a trace amount of an impurity phase was found along with a pyrochlore phase with a lattice constant larger than the $x = 0.4$ phase. A plot of lattice constant, a_0, versus x is linear from $x = 0.0$ to $x = 0.5$ indicating that a well-behaved solid solution exists within this range (Fig. 1). Attempts to prepare solid solutions for $x > 0.5$ produced the $x = 0.5$ pyrochlore with increasing amounts of impurities.

Results of the chemical analysis for $x = 0.0$ to $x = 0.4$ are shown in Table I. The agreement between theory and observation is satisfactory except for $x = 0.4$ for which the results suggests a slight degree of oxidation.

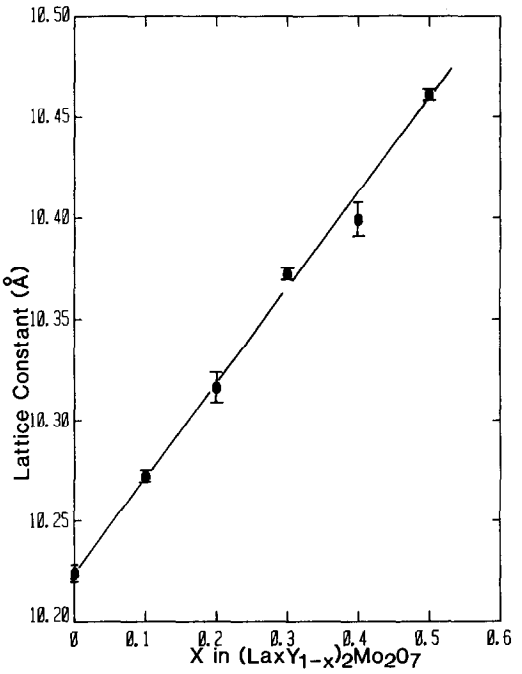

FIG. 1. Cell constants, a_0, for the solid solutions $(La_xY_{1-x})_2Mo_2O_7$ versus composition.

The magnetic properties of the solid solution series parallel those of $Y_2Mo_2O_7$, but there are some interesting systematic variations. In Fig. 2 are plotted the inverse susceptibility for the temperature range from 180 to 4.2 K along with the $x = 0$ case for comparison. All compositions exhibit Curie-Weiss behavior at sufficiently high temperatures with a broad minimum near 20–25 K and deviations from Curie-Weiss behavior at temperatures well above the minimum (in most cases). The Curie-Weiss

TABLE I

RESULTS OF Mo^{4+} CONTENT BY TGA AND TITRATION METHOD FOR $(La_xY_{1-x})_2Mo_2O_7$

Composition x	TGA[a] (wt. gain %)			Titration[b] (wt%)		
	Theor.	Obser.	Diff%[c]	Theor.	Obser.	Diff%[c]
0.0	6.64	6.77	−1.96	39.8	40.2	−1.01
0.1	6.51	6.54	−0.46	39.0	38.9	+0.26
0.2	6.38	6.42	−0.63	38.2	38.8	−1.57
0.3	6.25	6.36	−1.76	37.5	38.0	−1.33
0.4	6.31	6.25	+0.95	36.8	35.4	+3.80

[a] Wt. gain of the following reaction $R_2Mo_2^{IV}O_7 + O_2 \rightarrow R_2Mo_2^{VI}O_9$.
[b] The method reported previously (9).
[c] {wt% (theor.) − wt%(obs.)} × 100/wt%(theor.).

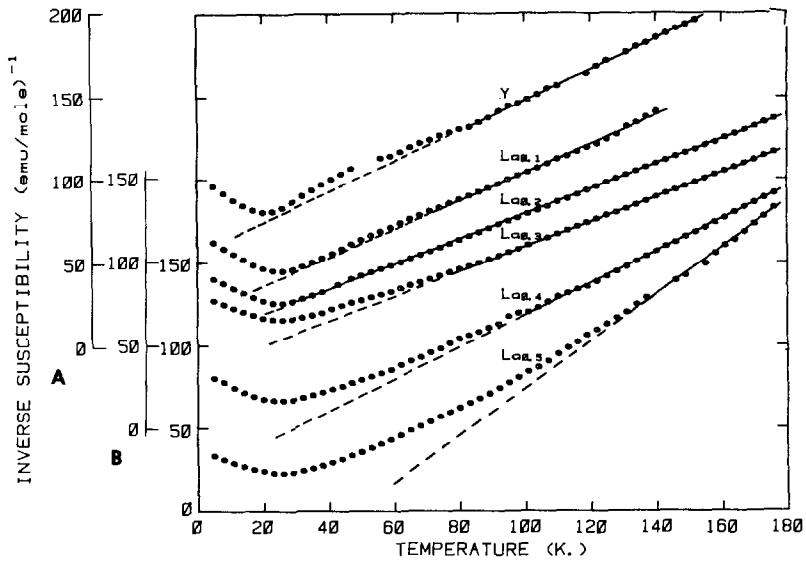

FIG. 2. Inverse magnetic susceptibility versus temperature for the solid solutions $(La_xY_{1-x})_2Mo_2O_7$. The curves have been displaced for clarity. Data for $x = 0$ $Y_{1.0}$) to $x = 0.3$ are referred to vertical axis *A*, those for $x = 0.4$ to axis *B*, and those for $x = 0.5$ to the remaining axis. The solid lines are Curie-Weiss fits and the fitting constants are listed in Table II.

constants, the temperature of the minimum (T_{ORD}), lattice constants, and other information are given in Table II.

Note first the striking increase in θ_c from -61 to $+41$ K as x goes from 0.0 to 0.5 and the lattice constant increases from 10.224(3) Å to 10.461(1) Å. This indicates the increasing importance of ferromagnetic exchange interactions as the average rare-earth radius increases. Such results parallel the behavior observed for the $R_2Mo_2O_7$ series and are plotted in Fig. 3 (*9*). In spite of the relatively large ferromagnetic exchange component in the $x = 0.4$ and $x = 0.5$ series members there is no transition to a ferromagnetic long-range ordered state as found for the $Sm_2Mo_2O_7$ and $Nd_2Mo_2O_7$ compounds with similar lattice constants.

Instead, all of the solid solution phases studied show spin-glass or cluster-glass behavior as does $Y_2Mo_2O_7$ (*10*). This is illustrated in Figs. 4 and 5 for the compositions

TABLE II

LATTICE CONSTANTS AND MAGNETIC DATA FOR $(La_xY_{1-x})_2Mo_2O_7$

x	Lattice const. (Å)	T_{ORD} (K)	θ (K)	Cm (per formula) (emu/mole K)	μ_{eff} (Mo^{4+}) (μ_B)	Remanence[a] (μ_B/Mo)
0	10.224(3)	22	−61	1.058	2.08	0.003
0.1	10.272(3)	25	−30	1.252	2.24	0.007
0.2	10.316(8)	25	−5	1.326	2.30	0.013
0.3	10.372(3)	25	+23	1.309	2.29	0.021
0.4	10.399(8)	24	+31	1.027	2.03	0.020
0.5	10.461(1)	22	+41	0.733	1.712	0.015

[a] Data taken at 4.2 K after sample was cooled in 1.0T field from high temperatures.

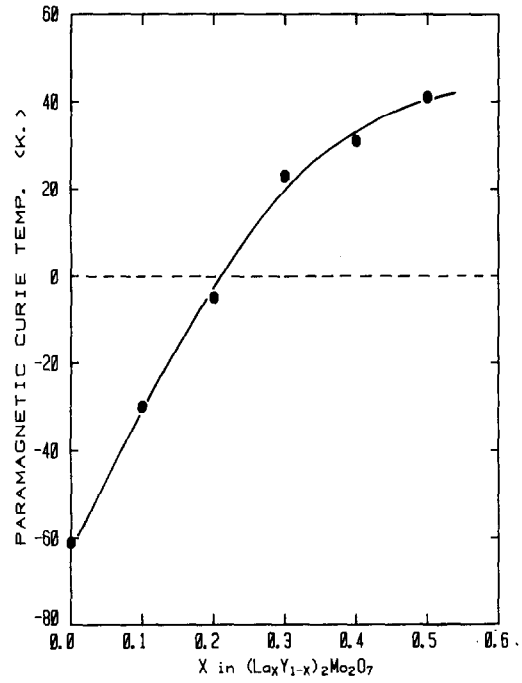

FIG. 3. The Weiss constant, θ_c, as a function of composition for the series $(La_xY_{1-x})_2Mo_2O_7$.

$(La_{0.3}Y_{0.7})_2Mo_2O_7$ and $(La_{0.2}Y_{0.8})_2Mo_2O_7$. Note the strong dependence on sample history for the susceptibility versus temperature data and the isothermal (4.2 K) magnetization data. All of the solid solution phases exhibit a remanent moment at 4.2 K upon demagnetization of the near zero-field (0.0045-T) cooled state. From Table II, this remanent moment increases with x. Similar to $Y_2Mo_2O_7$, these compounds represent a rare case of spin-glass behavior in concentrated systems with no apparent disorder on the magnetic sublattice. Only a few examples such as $EuSe_{0.9}S_{0.1}$ (*12*) and $Cd_{0.5}Zn_{0.5}Cr_2S_4$ (*13*) are known. For the solid solutions, unlike $Y_2Mo_2O_7$, there is obvious disorder on the diamagnetic sites. However, as for $Y_2Mo_2O_7$, there exist as yet no detailed structural studies and a discussion of the origin of the spin-glass properties should, at least, await structural information.

Summary and Conclusions

The Weiss constant, θ_c, for the $(La_xY_{1-x})_2Mo_2O_7$ pyrochlores changes sign from negative to positive as the average size of the R-atom increases. Assuming that θ_c measures the algebraic sum of all of the Mo–Mo exchange interactions this supports the argument that a competition between ferromagnetic and antiferromagnetic exchange, i.e., frustration, exists for all R and that the balance can be tipped by manipulating the size of R. In all cases where R is diamagnetic (R = Y or La_xY_{1-x}) spin-glass or cluster-glass behavior is observed at low temperatures with no long-range order regardless of the effective R radius or the existence of a net positive θ_c. This is an unusual result for crystalline systems in

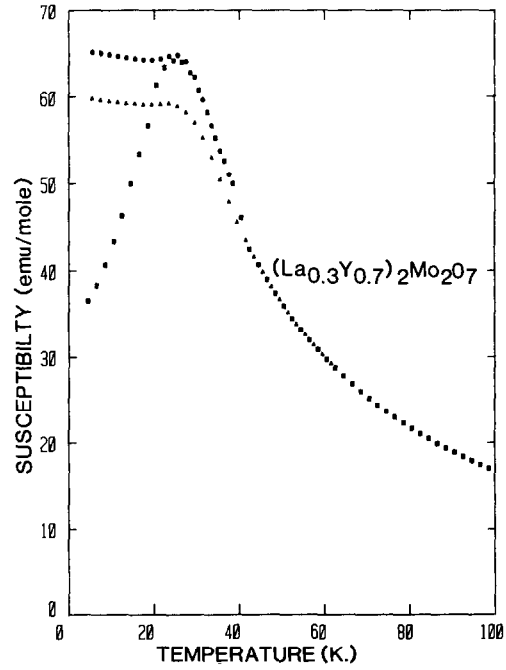

FIG. 4. Susceptibility versus temperature for $(La_{0.3}Y_{0.7})_2Mo_2O_7$ for the same sample under different measurement conditions. □, Cooled in a zero field, measured in a 0.4-T field; ○, cooled in a 0.4-T field, measured in a 0.4-T field; ▲, cooled in a 1.0-T field, measured in a 1.0-T field.

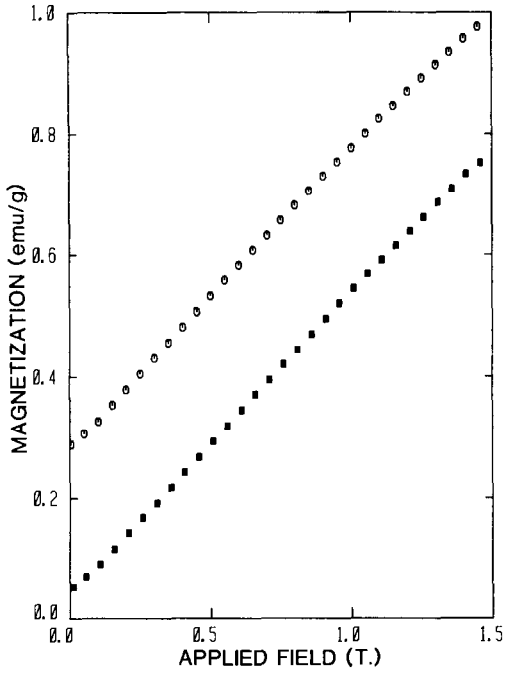

FIG. 5. Demagnetization versus field curve for $(La_{0.2}Y_{0.8})_2Mo_2O_7$ at 4.2 K. ■, sample cooled in zero field; ○, sample cooled in a 1.0-T field.

which the magnetic sublattice is concentrated and not obviously disordered. The origin of the spin-glass-like behavior is unclear and further studies are on-going.

The observations help to understand the absence of long-range magnetic order in the $R_2Mo_2O_7$ phases, R = Tb → Yb (*9*). However, it is now difficult to explain the presence of ferromagnetism for R = Nd, Sm, and Gd as the La_xY_{1-x} phases with similar lattice constants are frustrated spin-glasses. It is possible that the R–Mo exchange interaction plays a role by stabilizing a ferromagnetic configuration on the Mo(IV) sublattice. A further point, possibly relevant here to be discussed in a subsequent publication, is that the phases R = Nd, Sm, and Gd are all metals while the R = Tb, Y, and $La_{0.3}Y_{0.7}$ are semiconductors. In the metallic state, the conduction electrons provide an additional long-range coupling mechanism, via the *RKKY* interaction, which may also contribute to the stabilization of a long-range ferromagnetic ground state.

Acknowledgments

We thank Mr. G. Hewitson for assistance with the magnetic measurements and Professor C. V. Stager for use of the magnetometer and valuable discussions. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

References

1. M. A. SUBRAMANIAN, G. ARAVAMUDAN, AND G. V. SUBBA RAO, *Prog. Solid State Chem.* **15,** 55 (1983).
2. H. W. J. BLOTE, R. F. WIELINGA, AND W. J. HUISKAMP, *Physica* **43,** 549 (1969).
3. L. SODERHOLM AND J. E. GREEDAN, *Mater. Res. Bull.* **14,** 1449 (1979).
4. G. V. BAZUEV, O. V. MARKAROVA, AND G. V. SHVEIKIN, *Russ. J. Inorg. Chem.* **23,** 345 (1978).
5. T. SHIN-IKE, G. ADACHI, J. SHIOKAWA, M. SHIMADA, AND MIKOIZUMI, *Mater. Res. Bull.* **14,** 1323 (1979).
6. H. FUJINIKA, N. KINOMURA, M. KOIZUMI, Y. MIYAMOTO, AND S. KUME, *Mater. Res. Bull.* **14,** 1133 (1979).
7. A. MANDIRAM AND J. GOPALAKRISHNAN, *Indian J. Chem. A.* **19,** 1042 (1980).
8. R. RANGANATHAN, G. RANGARAJAN, R. SRINIVASAN, M. A. SUBRAMANIAN, AND G. V. SUBBA RAO, *J. Low-Temp. Phys.* **52,** 481 (1983).
9. M. SATO, XU YAN, AND J. E. GREEDAN, *Z. Anorg. Allg. Chem.* **540/541** 177 (1986).
10. J. E. GREEDAN, M. SATO, AND XU YAN, *Solid State Commun.* **59** 895 (1986).
11. P. W. SELWOOD, "Magnetochemistry," 2nd ed. p. 78, Interscience, New York, 1956.
12. K. WESTERHOLD AND H. BACH, *J. Magn. Magn. Mater.* **28,** 214 (1982).
13. E. AGOSTINELLI, P. FELOCI, D. FIORANI, AND E. PAPARAZZO, *Solid State Commun.* **56,** 541 (1985).