Inorganic Chemistry, Vol. 13, No. 11, 1974 **2715**

Contribution from the Department of Chemistry,
Polytechnic Institute of New York, Brooklyn, New York 11201

Scheelite-Type Rare Earth Molybdates(V) and -(VI). Eu_xMoO_4 and $LnMoO_4$

E. BANKS* and M. NEMIROFF

Received April 2, 1974

AIC402191

New tetragonal scheelite-type compounds of stoichiometry $Eu^{II}{}_xMoO_4$ ($0.67 \leqslant x \leqslant 1.00$) and $Ln^{III}MoO_4$ (Ln = Y, Gd–Lu) have been prepared by heating reaction mixtures in sealed tubes. The series Eu_xMoO_4 changes from $Eu^{II}Mo^{VI}O_4$ to $Eu^{III}{}_{0.67}Mo^{VI}O_4$ with evidence from ir spectra and lattice parameter shifts of distortion and multiple site symmetry of the $MoO_4{}^{2-}$ tetrahedra. Density measurements indicate that the solid solutions are characterized by Eu lattice vacancies. The $Eu_{0.67}MoO_4$ is readily converted to the monoclinic $Eu_2(MoO_4)_3$ structure, an ordered vacancy modification of the scheelite structure. Infrared spectra and lattice parameter shifts of the $LnMoO_4$ phases are compatible with the distribution Ln^{III}-Mo^VO_4. Magnetic susceptibility measurements on $YMoO_4$ and $GdMoO_4$ show an effective moment of 1.31 μ_B for Mo^V. This is reduced from the spin-only value of 1.73 μ_B for d^1 by spin–orbit coupling. These are the first compounds reported in which all the Mo is present as Mo^VO_4 tetrahedra.

Introduction

Preparations of mixed oxides of the rare earths and group VI transition elements nominally in the 5+ oxidation state have led to strikingly different results in the cases of chromium and tungsten. In the latter case, the products are tungsten bronzes Ln_xWO_3 ($0 < x < 0.33$)[1] while chromium forms compounds of huttonite or zircon structures,[2] with composition $LnCrO_4$, where the chromium is present in the form of distorted $CrO_4{}^{3-}$ tetrahedra with a chromium valence of 5+. These compounds are isostructural with the corresponding phosphates, arsenates, and vanadates.[3] The arsenates and vanadates are reported to transform at high pressure to a scheelite-type phase which can be quenched and retained metastably at 1 atm.[4] Stubican has found that rare earth niobates, $LnNbO_4$, and tantalates, $LnTaO_4$, transform to a high-temperature nonquenchable scheelite-type phase.[5] At the time this research was undertaken, there were no reports of reduced molybdenum rare earth oxides, nor was there any report of compounds containing pentavalent molybdenum in $MoO_4{}^{3-}$ anions. Recently a report of Na_3MoO_4 has appeared,[6] but its structure is not yet known, although the authors suggest a structure derived from the rock salt structure. In a dissertation by Hubert,[7] structures of the type $Ln_5Mo_3O_{16}$ were reported. The susceptibility measurements were compatible with $Ln_5Mo^{VI}{}_2Mo^VO_{16}$. In the present work, we offer evidence that all the molybdenum in the $LnMoO_4$ compounds is in the 5+ oxidation state and that, in the defect solid solutions involving europium, it remains in the form of molybdate(VI) anions.

Experimental Section

The Eu_xMoO_4 compounds were prepared by heating a mixture of the appropriate molar ratios of MoO_2, MoO_3, and Eu_2O_3 in evacuated and sealed silica tubes for 1–2 hr at 1200° except for $Eu_{0.80}MoO_4$ which was heated for 2 hr at 1050°. The compounds were deep brown-black except for $Eu_{0.70}MoO_4$ and $Eu_{0.67}MoO_4$ which were gray. McCarthy has reported the preparation of $EuMoO_4$.[8] The $LnMoO_4$ compounds were prepared by heating thoroughly mixed equimolar ratios of MoO_2, MoO_3, and Ln_2O_3 at 1200° for 1 hr in evacuated and sealed silica tubes. The compounds are all black. Attempts at preparing $LaMoO_4$–$SmMoO_4$ were unsuccessful. The preparations were black. However, the powder patterns were quite similar to those of the starting rare earth oxides Ln_2O_3. The oxides used were Baker and Adamson MoO_3 (99.5% minimum), Alfa Inorganics MoO_2 (99% minimum), and ROC/RIC rare oxides (99.9% minimum).

Lattice parameter measurements for all powders were calculated by a least-squares program from data taken with graphite-monochromated Cu Kα radiation using W or Si as internal standards. The infrared measurements were taken on a Perkin-Elmer Model 521 spectrophotometer. Samples were pressed in KBr pellets with the exception of $Eu_{0.67}MoO_4$ which was ground in Nujol and placed between KBr disks. $Eu_{0.67}MoO_4$ would convert to the stable monoclinic $Eu_2(MoO_4)_3$ phase when pressed in KBr pellets. Density measurements of $Eu_{0.90}MoO_4$, $Eu_{0.80}MoO_4$, and $GdMoO_4$ were measured by displacement of water. The magnetic susceptibility measurements of $YMoO_4$ and $GdMoO_4$ were obtained on a vibrating-sample magnetometer from room temperature to liquid nitrogen temperature.

Lattice Parameter Measurements

Lattice parameters for the $LnMoO_4$ and Eu_xMoO_4 compounds are shown in Tables I and II, respectively. A plot of $V^{1/3}$ *vs.* r for Ln^{3+} eight-coordinate rare earth radii[9] is linear within experimental error except for Ho^{3+} and Y^{3+} (Figure 1). The poor fit at Ho^{3+} and Y^{3+} is most likely due to uncertainties in the reported ionic radii. Greis and Petzel[9] calculated ionic radii for ${}^{VIII}Y^{3+}$ and ${}^{VIII}Ho^{3+}$ as 1.004 and 1.000 Å, respectively. However, extensive data on rare earth Al, Ga, and Fe garnets[10] show differences in lattice parameters of no more than one part per thousand for Y^{3+} and Ho^{3+} garnets, indicating that the ionic radii of ${}^{VIII}Y^{3+}$ and ${}^{VIII}Ho^{3+}$ are closer than the difference indicated by Greis and Petzel for the trifluorides. A plot of V *vs.* x for Eu_xMoO_4 drawn in Figure 2 shows more deviation from a straight line than the plot of Figure 1. This is probably due to the uncertainty in the stoichiometry of europium. The rare earth molybdates (Y, Gd–Lu) do not exhibit this nonstoichiometry. Attempts to synthesize Y_xMoO_4 and Gd_xMoO_4 where $x < 1.00$ resulted in the stoichiometric phase plus the expected impurities. Density measurements on $Eu_{0.80}MoO_4$ and $GdMoO_4$, shown in Table III, agree within experimental error with the X-ray density. The low densities of $Eu_{0.90}MoO_4$ and $YMoO_4$ are most likely due to voids between crystallites. Both compounds are soft sinters at the temperature of preparation. This indicates that the assumed stoichiometry of the Eu_xMoO_4 compounds is correct and can be formulated as $Eu_x\square_{1-x}MoO_4$.

Infrared Measurements

Infrared spectra of $EuMoO_4$ and $SrMoO_4$ shown in

---

(1) W. Ostertag, *Inorg. Chem.*, **5**, 758 (1966).

(2) H. Schwarz, *Z. Anorg. Allg. Chem.*, **323**, 275 (1963).

(3) H. Schwarz, *Z. Anorg. Allg. Chem.*, **323**, 33 (1963).

(4) V. S. Stubican and R. Roy, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **119**, 90 (1963).

(5) V. S. Stubican, *J. Amer. Ceram. Soc.*, **47**, 55 (1964).

(6) H. Kessler, C. Ringenbach, L. Lavielle, and A. Hatterer, *C. R. Acad. Sci., Ser. C.*, **277**, 763 (1973).

(7) P.-H. Hubert, Thesis, l'Universite Claude Bernard, Lyon I, France, 1973.

(8) G. J. McCarthy, *Mater. Res. Bull.*, **6**, 31 (1971).

(9) O. Greis and T. Petzel, *Z. Anorg. Allg. Chem.*, **403**, 1 (1974).

(10) M. Kokta, Thesis, Department of Chemical Engineering, Newark College of Engineering, Newark, N. J., 1972.

Table I. Lattice Parameters for Tetragonal $LnMoO_4$[a]

	a, Å	*c*, Å	*V*, Å^3
$YMoO_4$	5.170 (1)	11.000 (4)	294.1 (2)
$EuMoO_4$	5.392 (2)	11.992 (5)	348.7 (3)
$Eu_{0.95}Gd_{0.05}MoO_4$	5.374 (2)	11.942 (6)	344.9 (2)
$Eu_{0.85}Gd_{0.15}MoO_4$	5.351 (2)	11.850 (6)	339.4 (2)
$Gd_{0.85}Eu_{0.15}MoO_4$	5.220 (1)	11.170 (2)	304.4 (1)
$GdMoO_4$	5.214 (2)	11.180 (6)	304.0 (3)
$TbMoO_4$	5.202 (1)	11.110 (2)	300.7 (1)
$DyMoO_4$	5.187 (1)	11.064 (4)	297.7 (1)
$HoMoO_4$	5.175 (1)	11.008 (4)	294.9 (1)
$ErMoO_4$	5.156 (1)	10.966 (4)	291.5 (2)
$TmMoO_4$	5.141 (1)	10.962 (3)	288.6 (1)
$YbMoO_4$	5.127 (1)	10.880 (2)	286.0 (1)
$LuMoO_4$	5.117 (1)	10.857 (3)	284.3 (1)

[a] Least-squares deviations in parentheses.

Table II. Lattice Parameters for Tetragonal Eu_xMoO_4[a]

	a, Å	*c*, Å	*V*, Å^3
$EuMoO_4$	5.392 (2)	11.992 (5)	348.7 (3)
$Eu_{0.90}MoO_4$	5.343 (3)	11.821 (5)	337.5 (3)
$Eu_{0.80}MoO_4$	5.299 (2)	11.769 (4)	330.6 (2)
$Eu_{0.70}MoO_4$	5.255 (4)	11.608 (9)	320.5 (5)
$Eu_{0.67}MoO_4$	5.232 (2)	11.528 (6)	315.6 (3)

[a] Least-squares deviations in parentheses.

Table III. Densities of Eu_xMoO_4, $YMoO_4$, and $GdMoO_4$

	Density, g/cm^3	
	Obsd	Calcd
$Eu_{0.80}MoO_4$	5.53-5.58	5.61
$Eu_{0.90}MoO_4$	5.40-5.53	5.83
$YMoO_4$	5.30-5.40	5.62
$GdMoO_4$	6.80-6.85	6.93

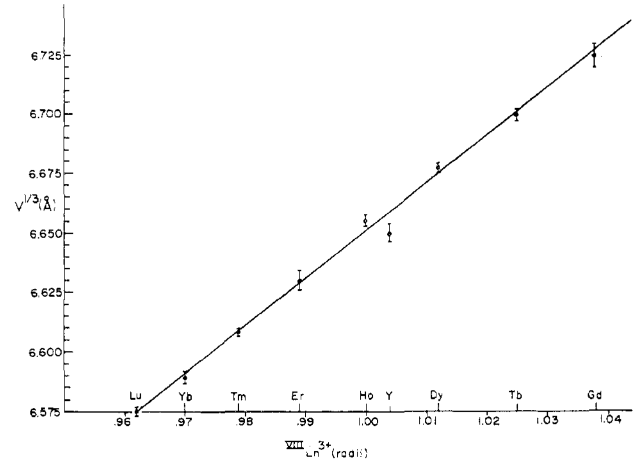

Figure 1. $V^{1/3}$ *vs.* eight-coordinate radii of Ln^{3+} ions[9] for $LnMoO_4$ compounds.

Figure 3 are very similar, as would be expected for $MoO_4{}^{2-}$ tetrahedra. The spectra of the europium-deficient Eu_xMoO_4 compounds show a distortion of the $MoO_4{}^{2-}$ tetrahedra. The band at 705 cm^{-1} increases in relative intensity with decreasing europium content. This is compatible with multiple-site symmetry for the $MoO_4{}^{2-}$ tetrahedra.

The spectrum of $GdMoO_4$ in Figure 4 is characteristic of all the $LnMoO_4$ compounds and is also similar to that of $GdNbO_4$, reported by Komkov[11] to contain tetrahedral $NbO_4{}^{3-}$ groups, which is also shown in Figure 4. This indicates that $Mo^VO_4{}^{3-}$ tetrahedra are present. Solid solutions of $Gd_{1-x}Eu_xMoO_4$ and $Eu_{1-x}Gd_xMoO_4$ were prepared where the solid solubility limits of x were both ~0.15. The infrared spectra of some of these solid solutions are shown in Figure 4. The spectrum of $Gd_{0.85}Eu_{0.15}MoO_4$ remains unchanged from that of $GdMoO_4$. This is a clear indication that Eu^{3+} enters the Gd^{3+} sites. If Eu^{2+} were to enter the sites, the presence of $Mo^{VI}O_4{}^{2-}$ would be necessary for charge compensation. No $MoO_4{}^{2-}$ vibrational modes are present in the spectrum. In addition, the cell volume is only slightly increased above that of $GdMoO_4$: 304.4 Å^3 *vs.* 304.0 Å^3, indicating substitution by Eu^{3+}, not Eu^{2+}. The case with $Eu_{0.85}Gd_{0.15}MoO_4$ is more confusing. Gd^{3+} must enter Eu^{2+} sites. This is confirmed by the substantial decrease in the cell volume compared with $EuMoO_4$: 339.4 Å^3 *vs.* 348.7 Å^3. The change in the infrared spectrum is most likely due to the presence of distorted $Mo^{VI}O_4{}^{2-}$ and $Mo^VO_4{}^{3-}$ tetrahedra. The strongest broad band of $Mo^VO_4{}^{3-}$ which would be expected at 650 cm^{-1} may be hidden under the broad band of a distorted $Mo^{VI}O_4{}^{2-}$ tetrahedron. The similarity between the spectra of $Eu_{0.85}Gd_{0.15}MoO_4$ and $Eu_{0.90}MoO_4$ suggests that there may be some $Mo^VO_4{}^{3-}$ present in the latter. However, the infrared measurements cannot resolve this uncertainty.

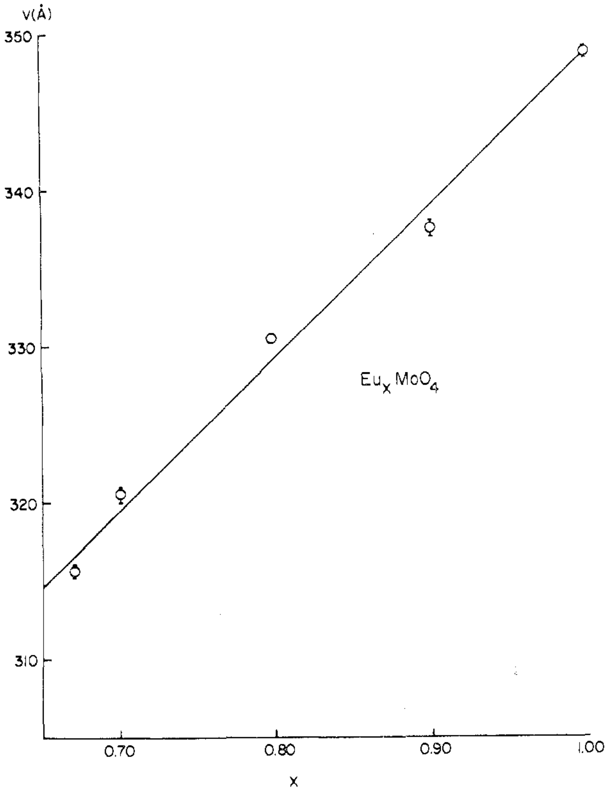

Figure 2. Volume *vs.* x in Eu_xMoO_4 compounds.

Magnetic Measurements

Magnetic susceptibility measurements have been made on $YMoO_4$ and $GdMoO_4$ in the temperature range 77-300°K. The plots of $1/\chi \times 10^{-2}$ ((emu)$^{-1}$) *vs.* T for $YMoO_4$ and $1/\chi$ ((emu)$^{-1}$) *vs.* T for $GdMoO_4$ are shown in Figures 5 and 6, respectively: for $YMoO_4$, $C_m = 0.213$ (1), $\mu_{eff} = 1.306$ (4) μ_B, $\theta = -62$ (1)°K; for $GdMoO_4$, $C_m = 8.175$ (8), $\mu_{eff} = 8.086$ (5) μ_B, $\theta = 0.3$ (2)°K.

If we assume the Mo^V contribution to the susceptibility remains unchanged, the Gd^{III} contribution to the Curie constant $C_{m(Gd)} = 7.86$. This compares favorably with the expected value for $J = 7/2$, $C_m = 7.88$.

The large negative deviation of the effective moment of Mo^V from the spin-only value of 1.73 μ_B is undoubtedly caused by spin-orbit coupling of the lowest lying state and the first excited state. The infrared spectrum of $GdMoO_4$

---

(11) H. I. Komkov, *Kristallografiya*, **4**, 830 (1959).

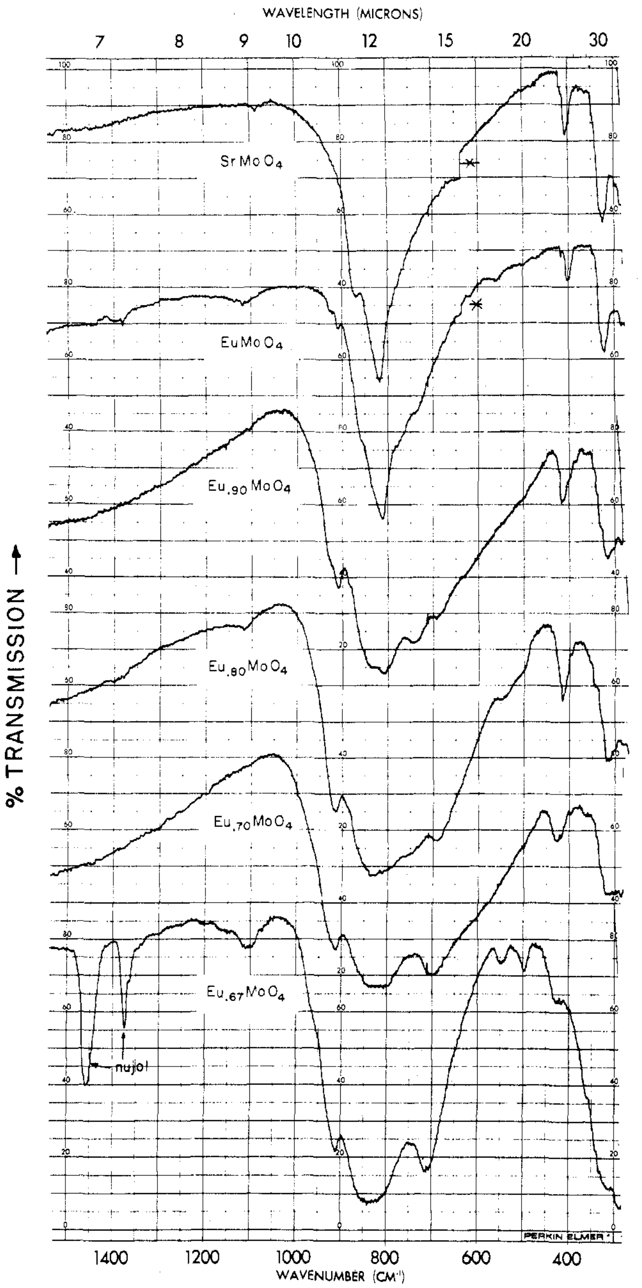

Figure 3. Infrared absorption of $SrMoO_4$ and Eu_xMoO_4 compounds taken in pressed KBr pellets. $Eu_{0.67}MoO_4$ was taken in a Nujol mull between KBr disks. An asterisk indicates filter change.

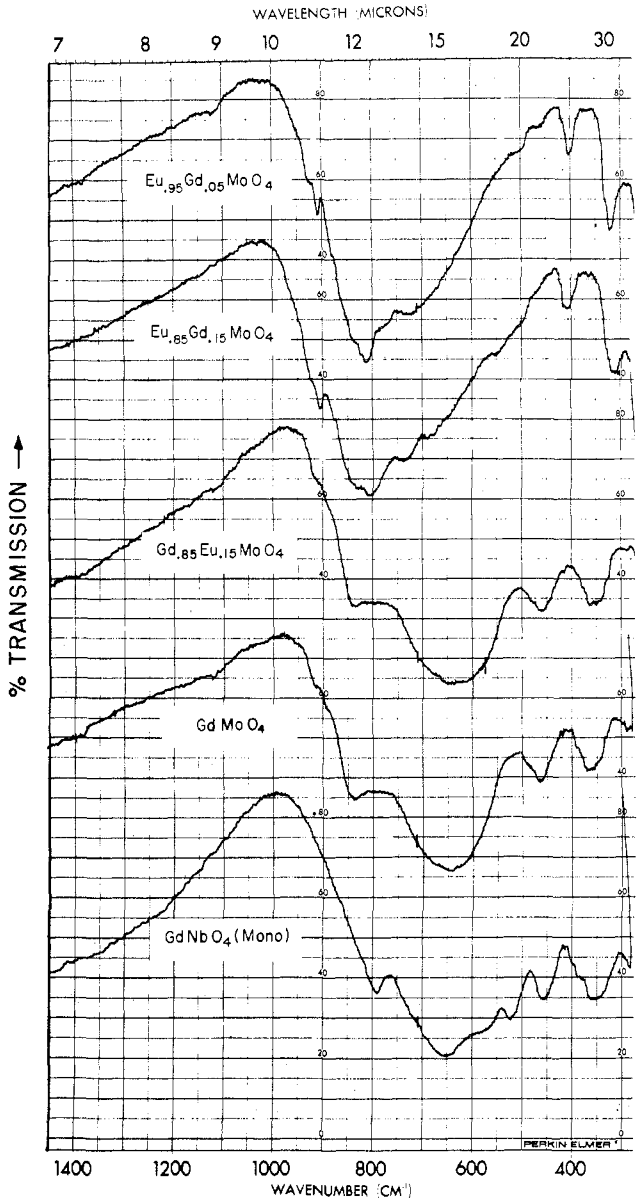

Figure 4. Infrared absorption of $Eu_{1-x}Gd_xMoO_4$ and $GdNbO_4$ (Mono = monoclinic).

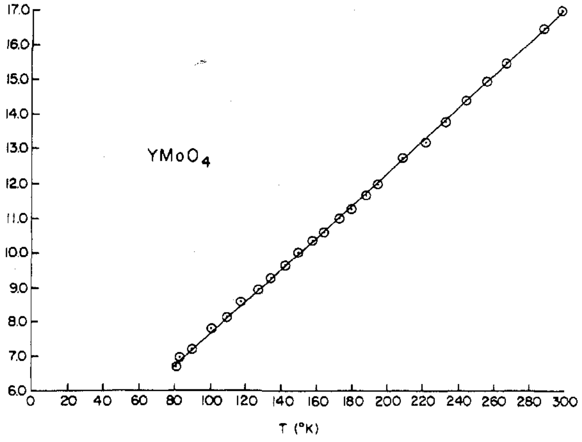

Figure 5. $1/\chi_m \times 10^{-2}$ ((emu)$^{-1}$) *vs.* *T* (°K) for $YMoO_4$.

indicates substantial distortion of the $Mo^VO_4{}^{3-}$ tetrahedron. Most likely the lowest ^2E state of an undistorted tetrahedron is split and the energy gap between this and the next excited state may not be large. The ground state is orbitally nondegenerate causing complete quenching of the ground-state orbital momentum contributions to the effective moment. In octahedral $AMoF_6$ (A = Na, K, Nb, Cs) the effective moment has been reported to be as low as 1.5 μ_B.[12] Since Δ (tetrahedral) = $^4/_9\Delta$(octahedral) for equivalent ligands, the crystal field splitting Δ for these tetrahedral molybdates is quite reduced from the octahedral $MoF_6{}^-$ case. In the case of a completely quenched ground-state orbital momentum $\mu_{eff} = \mu_{so}(1 - \alpha\lambda/\Delta)$,[13] where μ_{so} is the spin-only moment, λ is the spin-orbit coupling constant, $\alpha = 2$ for the d^1 case, and Δ is the crystal field splitting parameter. Dunn[14] has

---

(12) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.,* 3776 (1958).

(13) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, London, 1960.

(14) T. M. Dunn, *Trans. Faraday Soc.,* 57, 1441 (1961).

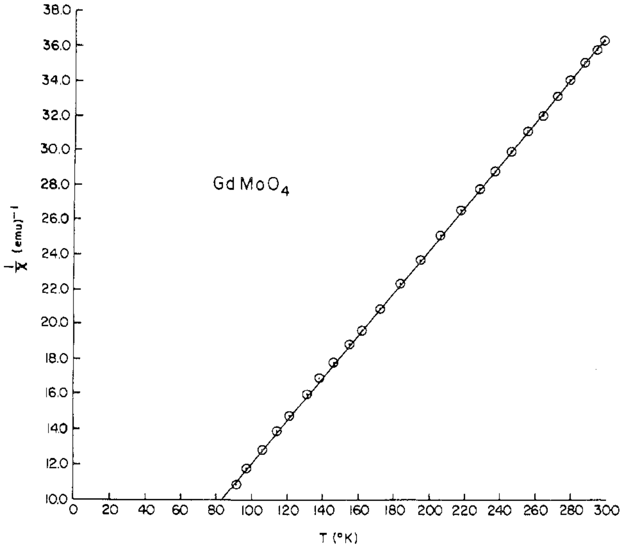

Figure 6. $1/\chi_m$ ((emu)$^{-1}$) *vs.* T (°K) for GdMoO$_4$.

calculated the spin–orbit coupling constant for the Mo^V free ion as 1030 cm^{-1}. The actual spin–orbit coupling constant for coordinated Mo^V is most likely reduced only slightly from this value due to the slight expansion of the electron cloud. If μ_{eff} for Mo^V in these compounds is 1.306 (4) μ_B and $\alpha\lambda/\Delta \approx 0.23$, this would require $\Delta \approx 9000$ cm^{-1}. Δ might be determined spectroscopically. However, these compounds are black and the spectrum from the infrared through the visible region is flat with the molybdates diluted in KBr pellets. It might be possible to dilute these compounds in a solid solution with an appropriate scheelite host. However no A^{III}B^{V}O$_4$ scheelite phases stable at room temperature are known with the exception of the high-pressure phases of the rare earth arsenates and vanadates.[4] It is also not certain that the distortion of the BO$_4$$^{3-}$ tetrahedra in these compounds is closely similar to that in the molybdates. It would be easier to dope these molybdates in rare earth niobates LnNb^{V}O$_4$ which crystallize in the monoclinic fergusonite structure. This is a distortion of scheelite.[11] In addition NbO$_4$$^{3-}$ has a similar tetrahedral distortion to those of the molybdates as indicated in its infrared spectrum in Figure 4.

Conclusions

Lattice parameter and density measurements on the solid solutions Eu$_x$MoO$_4$ indicate that the molybdenum remains in the 6+ oxidation state and that the vacancies are compensated by the presence of Eu^{3+} resulting in the formula Eu$^{II}{}_{1-3x}$Eu$^{III}{}_{2x}\square_x$MoO$_4$. Although the infrared spectra of these phases appear to support this formulation, with the appearance of broadening and extra peaks indicating the presence of multiple sites, the presence of some MoO$_4$$^{3-}$ cannot be completely ruled out. The increase in absorption in the region of the main peak of MoO$_4$$^{3-}$ cannot be attributed to that anion, but it is possible that it may be making some contribution in concentrations too low to permit the appearance of a peak at 650 cm^{-1}. The poor resolution of these spectra and the inability to obtain Raman spectra have precluded any attempt at more detailed analysis.

The disordered scheelite structure of Eu$_{0.67}$MoO$_4$ appears to be similar to that of the high-temperature phase which was suggested to exist above 848° by Jeitschko,[15] who reported that single crystals of La$_2$(MoO$_4$)$_3$ grown by the Czochralski method fractured on cooling through that temperature. This was attributed to a disorder–order transition. Our Eu$_{0.67}$MoO$_4$, quenched from 1200°, transformed to the ordered structure of Eu$_2$(MoO$_4$)$_3$ on grinding with KBr. This indicated it was metastable.

The LnMoO$_4$ compounds clearly contain MoO$_4$$^{3-}$, with no evidence for MoO$_4$$^{2-}$ in the infrared spectra. The significant decrease in lattice parameters relative to EuMoO$_4$ and the similarity of the infrared spectra of GdNbO$_4$ and GdMoO$_4$ all strongly confirm the formulation. The infrared spectrum of GdNbO$_4$ essentially agrees with that of YNbO$_4$ previously reported.[16] The cell volume of the high-temperature scheelite form of GdNbO$_4$ has been reported[17] as 306.2 Å^3 measured at 850° which is quite close to our value of 304.0 Å^3 for GdMoO$_4$ taken at room temperature. In addition, the isostructural relation of all members of the series, including YMoO$_4$, and the regular decrease in lattice parameters following the lanthanide contraction leave little room for doubt. These compounds appear to be the first in which the MoO$_4$$^{3-}$ anion has been reported as the only molybdenum species present.

The growth of single crystals of the intermediate Eu$_x$MoO$_4$ phase would be of considerable interest, especially if ordered low-temperature phases could be prepared at certain compositions. Flux methods would probably be necessary; samples with $x > 0.67$ melted incongruently. The LnMoO$_4$ compounds decomposed to mixtures of Ln$_2$(MoO$_4$)$_3$, MoO$_2$, and Ln$_2$O$_3$ at high temperatures, and low-melting flux techniques might be the only possibility for successful growth.

The reduced moment of Mo^V (4d^1) in YMoO$_4$ and GdMoO$_4$ can be attributed to spin–orbit coupling. It would be useful to be able to determine the splitting parameter Δ spectroscopically, preferably in a dilute system. The rare earth niobates LnNbO$_4$ would be a first choice as the host for these materials.

Acknowledgment. We wish to thank Professor Aaron Wold and Dr. J. J. Steger of Brown University for making the magnetic measurements. This work was sponsored by the U. S. Army Research Office (Durham, N. C.), Grant No. DA-ARO-D-31-124-72-G-7, and the Joint Services Electronic Program under Contract No. F44620-69-C-0047.

Registry No. YMoO$_4$, 52322-39-1; EuMoO$_4$, 22206-17-3; GdMoO$_4$, 52322-34-6; TbMoO$_4$, 52322-37-9; DyMoO$_4$, 52322-32-4; HoMoO$_4$, 52322-35-7; ErMoO$_4$, 52322-33-5; TmMoO$_4$, 52322-38-0; YbMoO$_4$, 52322-40-4; LuMoO$_4$, 52322-36-8; Eu$_x$MoO$_4$, 52322-41-5.

(15) W. Jeitschko, *Acta Crystallogr., Sect. B*, **29**, 2074 (1973).
(16) G. Blasse, *J. Solid State Chem.*, **7**, 169 (1973).
(17) K. A. Gingerich and H. E. Blair, *Advan. X-Ray Anal.*, **7**, 22 (1964).