

Figure 3. EHMO orbital diagrams and their irreducible representations in  $C_{2v}$  (eclipsed) and  $C_{2h}$  (staggered) of  $P_2H_4$ .

Therefore we artificially compressed this curve with an energy scale factor of 0.6 to increase the population of trans species. The resulting simulated spectrum is shown in Figure 2A as a broken line, and bands attributed to the trans isomers are indicated "t".

Assuming an approximately parallel shift of lone-pair energies upon replacement of H by methyl groups (compare to  $N_2H_4$ ,  $N_2Me_4^{2-4}$ ) or by F atoms (the perfluoro effect should equalize  $\Delta n_p$  gaps of "trans-only"  $P_2H_4$  and  $P_2F_4$  molecules due to pseudo- $\pi$  symmetry,  $C_{2h}$ ), the  $n_+(t)$  combination of *trans*-diphosphine is assigned to the band at 11.5 eV overlapped by  $\sigma$ - and  $\pi$ -orbital ionizations. The  $n_-(t)$  combination is then responsible for the low-energy asymmetry of the first band (Figure 1).

It seems that the sufficient separation of lone-pair ionization energies of different rotamers makes diphosphine a good example for making PE studies of temperature-dependent changes in conformer populations as well as for checking the quality of computed rotational barriers.

Registry No.  $P_2H_4$ , 13445-50-6.

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and the Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

## Magnetic Properties of the Divalent Europium Scheelites $EuMoO_4$ and $EuWO_4$ and the Mixed-Valence Phases $Eu_xMoO_4$ and $Eu_xWO_4$

J. E. Greedan,\* Richard G. Johnston, and Gregory J. McCarthy

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Previous reports of the magnetic behavior of the scheelite phase  $EuWO_4$  are in conflict. Shafer<sup>1</sup> observed paramagnetic behavior down to 1.6 K with  $\Theta_c = 0$  K but few details are given. Houlihan et al.<sup>2</sup> have reported some evidence of magnetic ordering with  $\Theta_c = +18$  K. We have restudied the magnetic properties of  $EuWO_4$  and the isostructural molybdate,  $EuMoO_4$ , in an effort to clarify the situation.

Included in our study are some members of the closely related phases  $Eu_xMO_4$  representing solid solution between  $EuMO_4$  and  $Eu_2(MO_4)_3$  ( $Eu_{0.667}MO_4$ ,  $M = W, Mo$ ) reported recently by Nemiroff and Banks<sup>3</sup> and Johnston and McCarthy.<sup>4</sup> These phases represent a unique type of mixed-valence europium oxide in which divalent and trivalent europium ions apparently occupy the same crystallographic site in the scheelite lattice. According to the criteria of Robin and Day<sup>5</sup> the existence of two different oxidation states of the same element in crystallographically equivalent sites leads to extensive electron-transfer effects between the ions. Compounds containing such species are predicted to have high electrical conductivities, strong magnetic exchange effects, and intense optical bands not present in the spectra of the isolated ions themselves (class IIIB behavior). On the other hand if the site coordination of the two ions is slightly different, i.e., different metal-ligand bond lengths, the electron-transfer effects are expected to be more limited but still discernible (class II behavior). It is of some interest to apply these criteria to the  $Eu_xMO_4$  phases.

## Experimental Section

**Preparation of Compounds.** The compounds were prepared as described in previous reports.<sup>4</sup> Briefly, for  $EuMO_4$  and  $Eu_2(WO_4)_3$  the starting materials consisted of appropriate weights of reagent grade oxides, powdered metals, and carbonates which were mixed, pelletized, and fired at 1050 °C for 48–130 h. The solid solutions were prepared by direct reaction between end members. Phases involving divalent europium were fired in sealed silica tubes at a low pressure of  $10^{-3}$  Torr.

**Magnetic Measurements and Diffuse Reflectance Spectra.** Magnetic data were collected using a PAR vibrating-sample magnetometer over the temperature range from 1.2 to 300 K. Calibration was done using  $Hg(Co(SCN)_4)$  and a small sphere of high-purity nickel. Samples consisted of pressed or sintered disks attached to the vibrating rod using low-temperature varnish.

Diffuse reflectance spectra were obtained using a Beckman DK-2A equipped with an integrating sphere and a  $BaSO_4$  standard.

## Results and Discussion

**$EuWO_4$  and  $EuMoO_4$ .** Results of susceptibility measurements were analyzed in terms of the Curie-Weiss Law. Molar Curie constants,  $C_M$ , were found to be 7.74 and 7.79 for  $EuWO_4$  and  $EuMoO_4$ , respectively. Note that the Curie constants are slightly less than the theoretical value, 7.87, indicating minor contamination by  $Eu^{3+}$  leading to actual compositions of  $Eu_{0.99}WO_4$  and  $Eu_{0.99}MoO_4$ . In contrast to previous reports  $\Theta_c = -5$  K for both compounds suggesting the possibility of antiferromagnetic exchange. As shown in Figure 1 (inset) no evidence of a Neel point can be observed

\* To whom correspondence should be addressed at McMaster University.

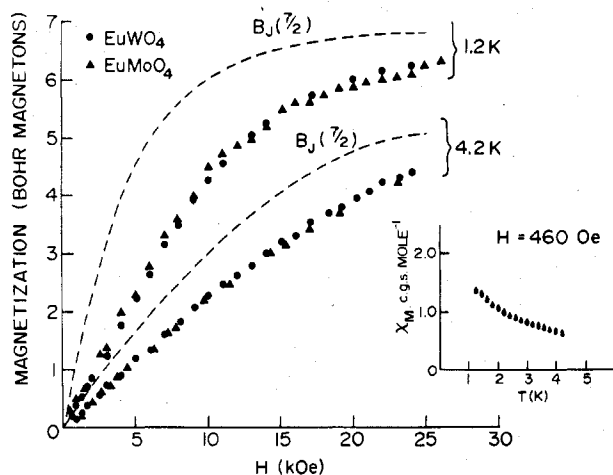


Figure 1. Isothermal magnetization curves for  $\text{EuWO}_4$  and  $\text{EuMoO}_4$  at 1.2 and 4.2 K compared with the Brillouin function for  $J = 7/2$ ,  $B_J(7/2)$ . Inset: temperature dependence of the susceptibility of  $\text{EuWO}_4$  and  $\text{EuMoO}_4$  at an applied field of 460 Oe.

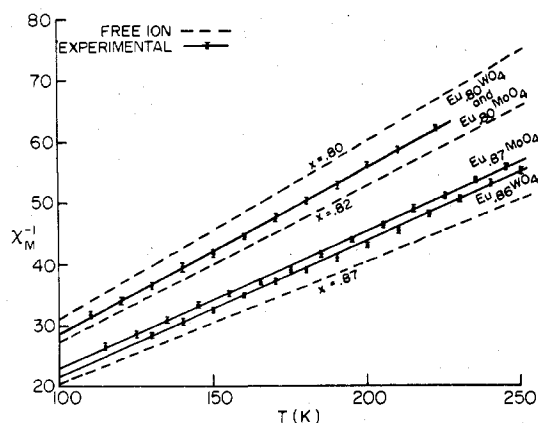


Figure 2. Inverse susceptibility as a function of temperature for  $\text{Eu}_{0.80}\text{WO}_4$ ,  $\text{Eu}_{0.80}\text{MoO}_4$ ,  $\text{Eu}_{0.86}\text{WO}_4$ , and  $\text{Eu}_{0.87}\text{MoO}_4$  compared with curves generated using free-ion values for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  for various  $x$  in  $\text{Eu}_x\text{MO}_4$ ,  $M = \text{W}, \text{Mo}$ .

down to 1.2 K for a relatively low applied field of 460 Oe. In addition the Mössbauer spectra of  $\text{EuWO}_4$  and  $\text{EuMoO}_4$  taken at 2 K show no evidence of hyperfine splitting.<sup>6</sup> However, the field dependence of the magnetization at 1.2 K, Figure 1, shows a linear behavior for both compounds up to about 10 kOe deviating considerably from the Brillouin function for  $J = 7/2$ . Field dependence data at 4.2 K, also Figure 1, show a Brillouin-like dependence for both compounds but the magnetization values are nearly 25% below those expected for a simple paramagnet. All of the above data suggest the importance of antiferromagnetic interactions in both of the  $\text{Eu}^{2+}$  scheelites with no evidence for long-range ordering to 1.2 K but evidence for short-range order up to 4.2 K.

**$\text{Eu}_x\text{WO}_4$  and  $\text{Eu}_x\text{MoO}_4$ .** Results of susceptibility measurements are shown in Figure 2 for  $\text{Eu}_x\text{WO}_4$ ,  $x = 0.80$  and 0.86, and  $\text{Eu}_x\text{MoO}_4$ ,  $x = 0.80$  and 0.87. The compositional parameter here is the nominal value based on the proportions of starting materials. These results can be fit reasonably well by assuming free-ion behavior for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . The magnetic behaviors for both ions are well-known.  $\text{Eu}^{2+}$  ( $L = 0$ ,  $S = 7/2$ ,  $J = 7/2$ ) compounds follow Curie-Weiss behavior with a molar Curie constant of 7.87 while the anomalous behavior of  $\text{Eu}^{3+}$  ( $L = S = 3$ ,  $J = 0$ ) has been recently discussed by Huang and Van Vleck.<sup>7</sup>

By comparing the experimental and theoretical (free-ion) susceptibility curves it is possible to determine the compo-

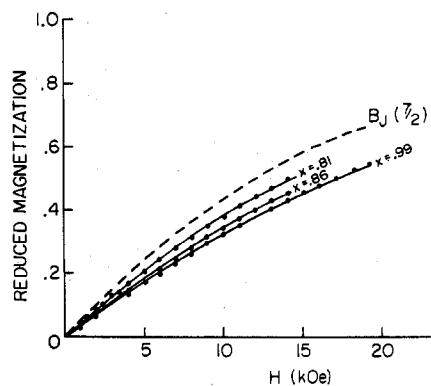


Figure 3. Reduced magnetization vs. applied field at 4.2 K for various compositions of  $\text{Eu}_x\text{WO}_4$  compared with the Brillouin for  $J = 7/2$ ,  $B_J(7/2)$ .

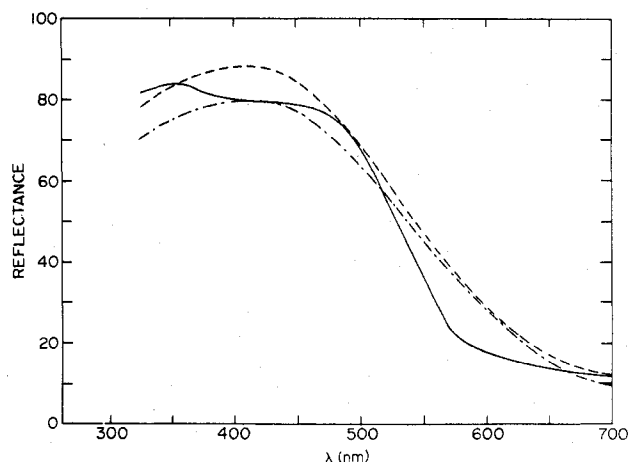


Figure 4. Diffuse reflectance data for various compositions of  $\text{Eu}_x\text{WO}_4$ : —,  $x = 0.99$ ; ---,  $x = 0.86$ ; - · -,  $x = 0.81$ .

sitional parameter with an accuracy comparable to that obtainable by standard analytical techniques.<sup>8</sup> For example the nominal compositions  $\text{Eu}_{0.80}\text{MO}_4$  ( $M = \text{Mo}, \text{W}$ ) are closer to  $\text{Eu}_{0.81}\text{MO}_4$ ;  $\text{Eu}_{0.87}\text{MoO}_4$  is actually  $\text{Eu}_{0.85}\text{MoO}_4$  while  $\text{Eu}_{0.86}\text{WO}_4$  is the actual composition to within experimental error. These discrepancies between the nominal compositions and those determined by the susceptibility measurements are not trivial when reckoned in terms of the mole percentage of  $\text{Eu}^{2+}$  as a  $\Delta x$  of 0.01 unit corresponds to 3 mol % of  $\text{Eu}^{2+}$ . As all of the solid solutions were prepared using the same batches of  $\text{EuMO}_4$  and  $\text{Eu}_{0.667}\text{MO}_4$ , it is clear that the final composition is a sensitive and apparently unpredictable function of the reaction conditions.

In Figure 3 we compare the field dependence of the reduced magnetization at 4.2 K for  $\text{Eu}_{0.81}\text{WO}_4$ ,  $\text{Eu}_{0.86}\text{WO}_4$ , and  $\text{Eu}_{0.99}\text{WO}_4$  with the Brillouin function for  $J = 7/2$ . Note that the negative deviations from ideal paramagnetic behavior decrease with increasing  $\text{Eu}^{3+}$  content (decreasing  $x$ ) indicating that  $\text{Eu}^{3+}$  serves only to dilute the  $\text{Eu}^{2+}$ - $\text{Eu}^{2+}$  exchange interactions. Qualitatively, this behavior is just that expected for a mixture of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions as at these temperatures all of the  $\text{Eu}^{3+}$  will essentially be in the  $J = 0$  ground state.

On the basis of this magnetic evidence the extent of electron transfer in the  $\text{Eu}_x\text{MO}_4$  phases is apparently limited to class II or possibly even class I behavior according to the Robin and Day criteria. In order to search for other evidence of electron-transfer effects we have also obtained diffuse reflectance spectra for  $\text{Eu}_{0.99}\text{MO}_4$ ,  $\text{Eu}_{0.81}\text{WO}_4$ , and  $\text{Eu}_{0.86}\text{WO}_4$  as shown in Figure 4. The visible spectra of  $\text{Eu}_{0.99}\text{WO}_4$  and the solid solutions are basically similar being dominated by a strong band centered roughly at 420 nm. This band is

probably due to the highly allowed  $4f^7$  to  $4f^65d^1$  transition which is typical for  $\text{Eu}^{2+}$  compounds.<sup>9</sup> There are some differences between the spectra of  $\text{Eu}_{0.99}\text{WO}_4$  and the mixed-valence species. For  $\text{Eu}_{0.99}\text{WO}_4$  the main absorption band is split with maxima at about 350 and 470 nm while the bands for the two solid solutions are not. Also the strong absorption falls off much more rapidly at long wavelengths for  $\text{Eu}_{0.99}\text{WO}_4$  than for the mixed-valence compounds. It is possible that these differences are simply due to the different crystal fields at  $\text{Eu}^{2+}$  in the "pure"  $\text{Eu}^{2+}$  phases and the mixed-valence phases as the  $4f^7$  to  $4f^65d^1$  transition is very sensitive to crystal fields.<sup>9</sup> For the mixed-valence phases one would expect a distribution of low-symmetry crystal field components due to the existence of cation vacancies and  $\text{Eu}^{3+}$  ions in the lattice which would broaden the  $\text{Eu}^{2+}$  absorption over that for a pure  $\text{Eu}^{2+}$  phase. Not shown in Figure 4 are the infrared spectra of the  $\text{Eu}_x\text{WO}_4$  phases which consisted of only three very weak bands at about 1830, 1960, and 2050 nm, which were also found in the spectrum of  $\text{Eu}_2(\text{WO}_4)_3$  and are attributed to the  $\text{Eu}^{3+}$  ion. These spectra show little unambiguous evidence for mixed-valence absorptions in  $\text{Eu}_x\text{WO}_4$ .

In summary bulk magnetic and optical absorption data on the mixed-valence compounds  $\text{Eu}_x\text{WO}_4$  show no clear evidence for extensive electron transfer or indeed any degree of electron transfer between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in spite of crystallographic data<sup>4</sup> which suggests that both ions occupy the same site in the scheelite structure.

Further measurements on these compounds should involve properties such as electrical resistivity and luminescence spectra which are also expected to be quite sensitive to electron transfer in order to determine more precisely the extent of mixed-valence interaction between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . It is possible that more detailed crystallographic work will reveal slightly different coordination environments for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in  $\text{Eu}_x\text{WO}_4$ .

However, it is also possible that the application of the Robin and Day criteria to mixed-valence lanthanide compounds is not quite so straightforward as in the case of mixed-valence compounds of the d-group elements. Referring to the notation of ref 5, the matrix element,  $V$ , which mixes the wave functions of the two oxidation states on different lattice sites will be very much smaller for 4f-group compounds than for d-group compounds owing to very small overlap between the 4f wave functions on adjacent sites compared to that of d wave functions. Thus, a mixed-valence lanthanide compound may exhibit very limited electron-transfer effects in spite of the fact that the two oxidation states are present in nearly equivalent sites,  $E_1 \approx 0$ , because the matrix element,  $V$ , is also very small.

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**Registry No.**  $\text{EuMoO}_4$ , 22206-17-3;  $\text{EuWO}_4$ , 13537-12-7;  $\text{Eu}_x\text{MoO}_4$ , 58384-31-9;  $\text{Eu}_x\text{WO}_4$ , 58384-32-0.

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from free-ion behavior is as large as 40% (which is true for  $\text{Eu}_2\text{O}_3$ , the worst case known to us), the uncertainty introduced into the total, theoretical susceptibility is only 2.4% while the experimental uncertainty is estimated at 2-3%.

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Contribution from the Chemistry Department,  
Technion-Israel Institute of Technology, Haifa, Israel

## Oxygen-17 Superhyperfine Tensor in Copper(II) Acetylacetonate

Daphne Getz and Brian L. Silver\*

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Superhyperfine interactions, as measured by ESR studies, can in principle reveal details of the electron distribution in the neighborhood of ligand atoms. In practice the number of ligands for which complete hyperfine tensors have been measured is small and most of the published data refer to nitrogen. The low value of  $\langle r^{-3} \rangle$  for  $^{14}\text{N}$  results in a comparatively small anisotropic tensor and most  $^{14}\text{N}$  superhyperfine tensors in the literature are nearly isotropic, with a consequent large uncertainty in the estimated population of the 2p orbital. For  $^{14}\text{N}$  atoms which are incorporated in organic ligands the hybridization is usually assumed to be  $sp^2$ , whether the full tensor is available or not. Recently the  $^{17}\text{O}$  and  $^{14}\text{N}$  tensors have been measured in a single-crystal study of copper(II) hydroxyquinolate.<sup>1</sup> The  $^{14}\text{N}$  tensor had been studied previously but the anisotropic component of the tensor appears to have been disregarded and the hybridization taken as  $sp^2$ . The  $^{17}\text{O}$  tensor was not analyzed in terms of orbital populations. Due to a larger gyromagnetic ratio and higher nuclear spin  $^{17}\text{O}$  splittings are generally larger and more accurately measurable than corresponding  $^{14}\text{N}$  splittings and can provide more reliable estimates of hybridization. Recently  $^{17}\text{O}$  superhyperfine interactions have been studied in a transition metal hydrate<sup>2</sup> and in oxide lattices.<sup>3</sup> In the present work we report the results of an ESR study in solution and in frozen solution of copper acetylacetonate enriched to 30 atom % in  $^{17}\text{O}$ .

The ESR spectrum of isotopically normal  $\text{Cu}^{\text{II}}\text{acac}$  was reported by McGarvey and Maki<sup>4</sup> and the g and Cu hyperfine tensors were found to be effectively axial. This is consistent with the near- $D_{4h}$  symmetry of the  $\text{CuO}_4$  unit as ascertained by x-ray structure analysis,<sup>5</sup> which gives an O-Cu-O bond angle of  $93.5^\circ$ , for the angle "outside" the chelate ring.

## Experimental Section

$^{17}\text{O}$ -enriched water was purchased from Yeda (Rehovot, Israel) and  $^{63}\text{Cu}$  (99.9 atom %) from Oak Ridge National Laboratory, Oak Ridge, Tenn. Acetylacetonate enriched to  $\sim 30\%$  in  $^{17}\text{O}$  was prepared by exchange with  $\text{H}_2^{17}\text{O}$  ( $\sim 35$  atom %) in the presence of  $\sim 0.01$  M  $\text{HClO}_4$ . Exchange is effectively complete within several minutes at room temperature.<sup>6</sup> Addition of anhydrous copper ( $^{63}\text{Cu}$ ) sulfate was followed by sodium bicarbonate to bring the pH to the alkaline range and by chloroform-toluene (1:1) to extract the complex. The resulting blue solution was dried over sodium sulfate. Spectra, in solution and in frozen solution, were taken at X band with a Varian V-4502 ESR spectrometer equipped with a variable-temperature accessory.

## Spectra and Results

**Solution.** The X-band ESR spectrum of  $^{17}\text{O}$ -enriched cupric acetylacetonate in chloroform-toluene (1:1) at room temperature is shown in Figure 1. The strong, and well-known,  $m_I$  dependence of the  $^{63}\text{Cu}$  hyperfine lines results in a very