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Communications

A New Magnetically Ordered Polymorph of CuMoO$_4$: Synthesis and Characterization of ε-CuMoO$_4$

Jaewook Baek,[†] Athena S. Sefat,[‡] David Mandrus,[‡] and P. Shiv Halasyamani*,[†]

Department of Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003, and Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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Magnetic behavior in metal oxides has been of great interest for a number of years.[1–5] Properties associated with magnetic behavior include ferro- and antiferromagnetism as well as magnetoresistance. Of great importance with all of these phenomena are the relationships between the physical property and the crystal structure. This is particularly true with cuprates. We have focused on the Cu^{2+}-d^0 oxide ternary system in order to examine if any magnetic ordering occurs, as well as investigate any interactions between the first-[6] and second-order[7–14] Jahn−Teller distortions in Cu^{2+} and the d^0 transition metal, respectively. One family where these phenomena may be examined is with Cu^{2+}−Mo^{6+} oxides, specifically CuMoO$_4$.

At least five different polymorphs of CuMoO$_4$ have been reported.[15–20] The stable polymorph under ambient conditions is triclinic, $P\bar{1}$, α-CuMoO$_4$,[15] that above 840 K transforms to hexagonal β-CuMoO$_4$ [16,17] It should be noted that for the β-phase, the space group and atomic coordinates were not reported. Below 200 K, γ-CuMoO$_4$ (also $P\bar{1}$) is stable.[20] Under pressure, two additional polymorphs have been reported, CuMoO$_4$-II and CuMoO$_4$-III ($P\bar{1}$ for both).[18,19] Both CuMoO$_4$-II and CuMoO$_4$-III are reported to have the distorted wolframite structure. In addition, a $p-T$ phase diagram for CuMoO$_4$ has been published by Wiesmann et al.[21] With respect to magnetic behavior, both α- and γ-CuMoO$_4$ do not exhibit any magnetic ordering down to 2 K, whereas CuMoO$_4$-II and CuMoO$_4$-III are antiferromag-

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[*] Corresponding author. E-mail: psh@uh.edu. Fax: (713) 743-0796.
[†] University of Houston.
[‡] Oak Ridge National Laboratory.

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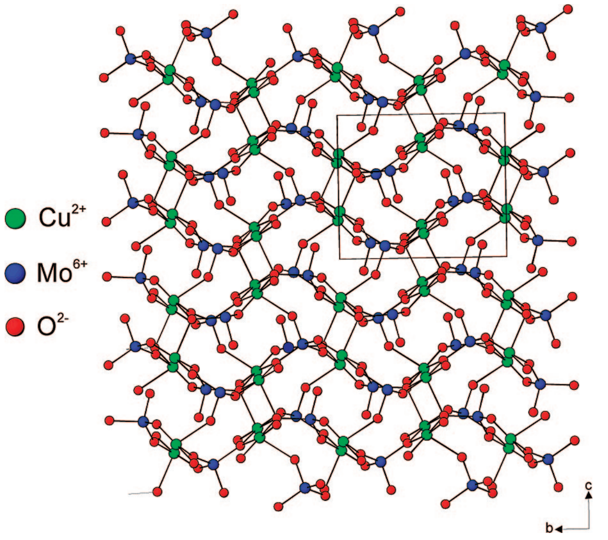

Figure 1. Ball-and-stick diagram of ε-$CuMoO_4$ in the *bc*-plane.

netic at low temperatures.[22,23] In this communication, we report on the synthesis and characterization of a new $CuMoO_4$ polymorph, ε-$CuMoO_4$ ($P2_1/n$). Magnetic susceptibility measurements indicate that the material orders magnetically, with a ferromagnetic component below $T_c \approx$ 10 K.

In our exploration of the Cu^{2+}−Mo^{6+}−oxychloride system, we synthesized ε-$CuMoO_4$ by placing a well-ground mixture of CuO, MoO_3, and $CuBr_2$ in a pyrex tube. The tube was evacuated, sealed, heated to 430 °C for 18 h, and cooled slowly to room temperature at 6 °C h^{-1}. Transparent green block-shaped crystals, subsequently determined to be ε-$CuMoO_4$, were recovered in 10% yield along with CuBr and α-$CuMoO_4$. Numerous attempts to synthesize ε-$CuMoO_4$ without $CuBr_2$ at different temperatures, heating and cooling rates, in air as well as under a vacuum, resulted in the formation of α-$CuMoO_4$. The exact role of $CuBr_2$ is unclear. A full description of the synthesis is given in the Supporting Information.

ε-$CuMoO_4$ exhibits a three-dimensional structure consisting of MoO_4 tetrahedra and CuO_5 square pyramids (Figure 1). The two unique Mo^{6+} cations are in tetrahedral coordination environments bonded to four oxygen atoms, with Mo−O bond distances ranging from 1.717(4)−1.895(3) Å. A second-order Jahn−Teller distortion is not observed in Mo^{6+} attributable to its tetrahedral coordination. The two unique Cu^{2+} cations are in square pyramidal coordination environments bonded to five oxygen atoms, with Cu−O bond distances ranging from 1.903(3)−2.368(4) Å. The sixth Cu−O contact is ~2.7 Å. In connectivity terms, the structure may be written as $\{[Cu(1)O_{2/4}O_{1/3}O_{2/2}]^{-1.667}[Cu(2)O_{1/4}O_{1/3}O_{3/2}]^{-2.167}[Mo(1)O_{1/4}O_{2/2}O_{1/1}]^{+1.5}\ [Mo(2)O_{3/2}O_{1/3}]^{+2.33}\}^0$.

One of the most interesting aspects of the structure is the occurrence of a "tetramer" of edge-shared CuO_5 square pyramids (Figure 2). The four equatorial Cu−O bonds within each square pyramid are substantially shorter than the Cu−O axial bond. The Cu−O equatorial bond distances range from 1.903(3) to 1.980(4) Å, whereas the CuO axial bonds are 2.368(4) and 2.391(4) Å. Thus, Cu^{2+} does exhibit a first-order Jahn−Teller distortion. One of the most novel aspects about the tetramer is that three of the edges are shared (Figure 2). Because of this edge-sharing, the Cu^{2+}−Cu^{2+} distances are quite close, ~2.96 and ~3.24 Å. The "tetramers" themselves are linked along the *a*, *b*, and *c*-axes by the MoO_4 tetrahedra (Figure 1), resulting in a three-dimensional topology. The Mo^{6+} tetrahedra are regular, with all of the oxygen atoms, except for O(5), bridging to at least one Cu^{2+} cation. O(5) bonds to Mo(2) in a terminal fashion, with a short Mo−O distance of 1.706(4) Å. Bond-valence calculations[24,25] resulted in values of 5.95 and 5.71 for Mo^{6+} and 2.01 and 2.12 for Cu^{2+}.

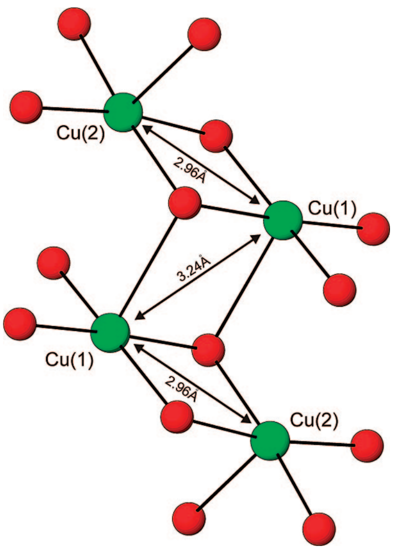

Figure 2. Ball-and-stick diagram of the CuO_5 square pyramidal tetramer in ε-$CuMoO_4$. Note that three of the edges are shared resulting in close Cu−Cu contacts.

Thermogravimetric measurements indicate ε-$CuMoO_4$ is thermally stable up to 700 °C. No weight loss is observed up to this temperature. Above 700 °C, a gradual weight loss is observed that continues up to the maximum temperature of our instrument.

The close Cu^{2+}−Cu^{2+} contacts suggested that magnetic measurements on ε-$CuMoO_4$ would prove interesting. Figure 3 shows the temperature dependence of the magnetic susceptibility measured under zero-field (zfc) and field-cooled (fc) conditions. The susceptibility is positive, rapidly increasing with decreasing temperature at ~12 K and separates to zfc and *fc* branches below 10 K. The $\chi(T)$ results are essentially isotropic in the paramagnetic state. The high-temperature susceptibility results measured in applied field of 1 T are shown in the inset of Figure 3. For temperatures above magnetic ordering, the $\chi(T)$ data were fitted to a modified Curie−Weiss law where $\chi = C/(T - \theta) + \chi_o$; *C* is the Curie constant, θ is the paramagnetic Weiss temperature, and χ_o is a temperature-independent term which incorporates contributions from Pauli and Van Vleck paramagnetism as well as from core and Landau diamagnetism. The fits to the data were done above 50 K. If the transition metal is the

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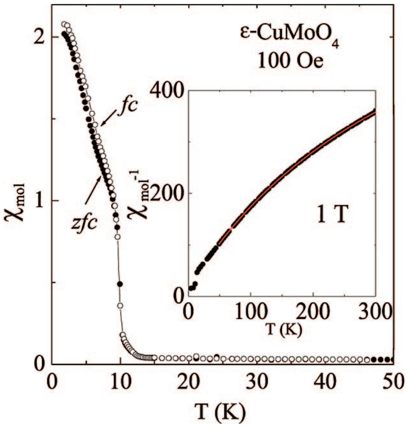

Figure 3. Temperature dependence of the magnetic susceptibility at 100 Oe in zfc and fc conditions. The inset is the inverse of susceptibility measured at 1 T and the fit to the Curie−Weiss above 50 K (in red).

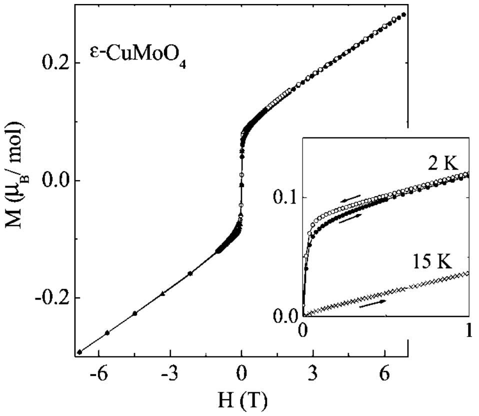

Figure 4. Field-dependent magnetization at 1.8 K. The inset shows the field dependence at 2 and 15 K.

only moment bearing ion, then the term C is related to the effective moment of the transition metal ion in paramagnetic state and $\mu_{\text{eff}} = g[S(S+1)]^{1/2}$. The paramagnetic effective moment, μ_{eff}, is 1.96 μ_B per formula unit that is close to the theoretically expected $\mu_{\text{eff}}/\text{Cu}^{2+}$ of 1.73 μ_B. The inferred Weiss temperature is −7.0(5) K, indicating weak antiferromagnetic exchange interactions between Cu ions. The temperature independent term is $\chi_o = 0.0012(1)$ mol^{-1}. Field dependent magnetization at 1.8 K is shown in Figure 4. The magnetization rises rapidly up to ~1000 Oe and changes weakly thereafter. The sample does not approach a saturated value at the highest field measured, as the magnetization at ~7 T is ~0.28 μ_B/f.u., far below the expected free ion magnetic moment value of 1 μ_B/Cu^{2+}. The field dependence of magnetization at 15 K is essentially linear (Figure 4, inset).

The precipitous rise in magnetic susceptibility at 100 Oe, as well as the noted hystereses (Figures 3 and 4), indicate that there is a ferromagnetic component to the ordered state in ε-CuMoO$_4$ and $T_c \approx 10$ K. The small ferromagnetic component may be the results of canted spin arrangements of copper and Dzyaloshinski−Moriya superexchange interactions. Neutron scattering measurements will be performed to confirm the ferromagnetic transition and the magnetic structure.

In summary, we have synthesized a new polymorph of CuMoO$_4$, ε-CuMoO$_4$. The material is magnetically ordered, at ~ 10 K, with a ferromagnetic component. Ongoing research involves scaling up the synthesis for variable neutron diffraction experiments, as well as expanding our synthesis into other d^0 transition metal−“magnetic” cation oxide systems.

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Supporting Information Available: Complete experimental and crystallographic details (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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