Title
Antiferromagnetic ordering of S=1/2 triangles in La$_4$Cu$_3$MoO$_{12}$

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Antiferromagnetic ordering of $S = \frac{1}{2}$ triangles in La$_4$Cu$_3$MoO$_{12}$


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Magnetic properties of a cupric triangular cluster compound La$_4$Cu$_3$MoO$_{12}$ were investigated. Susceptibility data show that paramagnetic cupric spin ($S = \frac{1}{2}$) above room temperature forms $S = \frac{1}{2}$ trimers at lower temperatures because of strong intratrimer antiferromagnetic interactions. The cluster moments acquire antiferromagnetic order below 2.6 K. The trimers can be polarized in an external field of 20 T at 1.3 K. The magnetization remains nearly constant at 1 $\mu_B$ per trimer up to a magnetization plateau at 55 T.

The spin quantum number (small, large, integer, half-integer) and the geometry of the magnetic sublattice affect the ground state of quantum antiferromagnets in various fashions. For example, spin singlet ground states with finite gaps to magnetic excited states have been found in several one-dimensional (1D) antiferromagnetic (AF) systems such as $S = \frac{1}{2}$ alternating bond chains, $S = \frac{1}{2}$ two-leg ladders, and $S = 1$ chains (Haldane systems). The discovery of inorganic model compounds such as CuGeO$_3$ (spin-Peierls), (VO)$_2$P$_2$O$_7$ (alternating chain), Y$_2$BaNiO$_5$ (Haldane), SrCu$_2$O$_3$, and Sr$_{14}$Cu$_{24}$O$_{41}$ (ladders) in the past decade has stimulated keen interest in such 1D systems. Their large AF interactions ($J$) and the thermal stability make it rather easy to finely tune the electronic properties of these materials by means of chemical doping. Spin gaps are also found in 2D systems such as CuV$_2$O$_9$ (Ref. 10) and SrCu$_2$(BO$_3$)$_2$.11

In the gapped ground states of these compounds, two neighboring $S = \frac{1}{2}$ spins form a spin singlet. On the other hand, AF trimer compounds are rare in nature. Sr$_3$Cu$_2$O$_4$ (three-leg ladder)7 is a specific example where the trimers on the rungs interact strongly with each other so that an analogy to a $S = \frac{1}{2}$ AF chain becomes valid. [Cr$_2$O(CH$_3$COO)$_6$(H$_2$O)$_3$]Cl$\cdot$6H$_2$O and [Fe$_2$O(CH$_3$COO)$_6$(H$_2$O)$_3$]Cl$\cdot$6H$_2$O (Ref. 12) comprise almost isolated triangular clusters with isotropic spins of $S = \frac{1}{2}$ and $\frac{1}{2}$, respectively, where strong intratrimmer AF interactions make the multiplet with $S_{\text{total}} = \frac{3}{2}$ the ground state. AF ordering owing to weak intertrimer interactions was observed at 0.15 K for the Fe salt.13 Here, we report on the magnetism of a cupric oxide in which AF $S = \frac{1}{2}$ trimers form a quasi-2D orthorhombic lattice.

La$_4$Cu$_3$MoO$_{12}$ is a layered compound with an average structure of the YAlO$_3$ type.14 The Cu$_3$MoO$_4$ layer of this compound shown in Fig. 1 can be derived from a triangular CuO layer by replacing a quarter of the Cu$^{2+}$ ions with non-magnetic Mo$^{5+}$ ions. One can consider the Cu$_3$MoO$_4$ layer as being made of Cu$_3$O triangular clusters as suggested from the bond lengths listed in Table I: The average Cu-O bond length within the triangle, 1.983 Å, is much shorter than that between neighboring triangles of 2.690 Å. The Cu$_3$MoO$_4$ layers are separated from each other by /O/La/O/ layers. The structure can be described as a quasi-2D orthorhombic lattice made of slightly distorted cupric ($S = \frac{1}{2}$) trimers. We have observed paramagnetism with $S_{\text{total}} = \frac{3}{2}$ below 250 K and AF ordering at 2.6 K. Moreover, an external magnetic field of 20 T induces a transition from the AF state to a spin-flop phase.

A powder sample was prepared by a solid state reaction of La$_2$O$_3$, CuO, and MoO$_3$. These were mixed in appropriate ratios, pressed into a pellet, heated at 1025 °C in air for 4
TABLE I. Selected bond lengths and angles for La$_4$Cu$_3$MoO$_{12}$.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond length (Å)</th>
<th>Atoms</th>
<th>Bond angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>intratriangle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1-O6</td>
<td>1.927</td>
<td>Cu1-O6-Cu2</td>
<td>123.61</td>
</tr>
<tr>
<td>Cu2-O6</td>
<td>1.916</td>
<td>Cu2-O6-Cu3</td>
<td>121.11</td>
</tr>
<tr>
<td>Cu3-O6</td>
<td>2.106</td>
<td>Cu3-O6-Cu1</td>
<td>115.28</td>
</tr>
<tr>
<td>intertriangle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1-O7</td>
<td>2.643</td>
<td>Cu1-O7-Cu2</td>
<td>102.48</td>
</tr>
<tr>
<td>Cu2-O7</td>
<td>2.800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1-O8</td>
<td>2.675</td>
<td>Cu1-O8-Cu3</td>
<td>105.05</td>
</tr>
<tr>
<td>Cu3-O8</td>
<td>2.842</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2-O5</td>
<td>2.780</td>
<td>Cu2-O5-Cu3</td>
<td>116.55</td>
</tr>
<tr>
<td>Cu3-O5</td>
<td>2.399</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

days with intermittent grinding, then cooled at 36 °C/h in the furnace to room temperature. Powder x-ray diffraction (XRD) showed no trace of impurities. Magnetic susceptibility was measured with superconducting quantum interference device (SQUID) magnetometers (Quantum Design MPMS equipped with a sample space oven and MPMS XL). Specific heat data were taken by means of a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS). High field magnetization was measured in a pulsed magnetic field up to 55 T by an induction method using a multilayer pulse magnet at KYOKUGEN, Osaka University.

Figure 2(a) shows the temperature dependences of magnetic susceptibility and its inverse measured on heating from 5 to 800 K in an external field of 1 T. The susceptibility above 400 K was fitted well to the Curie-Weiss law with $\mu_{\text{eff}} = 1.81$ (g = 2.09) and a Weiss temperature (θ) of −558 K. On the other hand, the slope of the 1/\(\chi - T\) plot below 250 K decreased to 0.39 times the high-temperature value. XRD data taken at several temperatures between 133 and 573 K did not indicate any structural transition, the lattice constants changing linearly with temperature. The small Curie constant (C) below 250 K indicates that each trimer has a total spin $S_{\text{total}} = \frac{1}{2}$. The large intratramer AF interactions give the large Weiss constant at high temperatures. The intertramer interactions seem to be weakly AF as suggested from the small Weiss constant of −16 K derived from the low temperature data. The observed susceptibility was consistent with a calculation assuming isolated equilateral triangles with a model Hamiltonian $H = J_1S_1S_2 + J_2S_2S_3 + J_3S_3S_1 + g\mu_B\mathbf{H}(S_1 + S_2 + S_3)$ where $J_1 = J_2 = J_3$ and $S_1 = S_2 = S_3 = \frac{1}{2}$.

As shown in Fig. 2(b), the best fit was obtained with $g = 2.17$ and $J = 813$ K and the Curie constant in the high temperature limit was three times the low temperature value. There is a discrepancy at low temperatures which is, most probably, because intertramer interactions were neglected in the calculation. We note that calculations for various types of distorted clusters did not lead to significant conclusion as shown later.

In the data measured in a field of 0.1 T down to 1.8 K shown in the inset of Fig. 2(a), a maximum appeared at 5 K and a kink at 2.6 K followed. The existence of the kink was clearly seen as a peak in the $d\chi/dT$ plot. As can be seen in Fig. 1 there is no spin frustration among the $S_{\text{total}} = \frac{1}{2}$ spins, so it is reasonable to assume that the anomaly results from AF order of spin trimers. The susceptibility maximum at 5 K can be attributed to short range order in the two-dimensional spin system.

Specific heat data were taken in zero field to investigate magnetism in further detail. Figure 3(a) shows the total specific heat divided by temperature plotted against temperature. The approximately $\lambda$-type anomaly at 2.6 K confirms magnetic ordering at this temperature. The solid line in Fig. 3(a) is an estimation of the lattice contribution from the data between 20 and 25 K expressed as $C_1 = \beta_1T^3 + \beta_2T^5$, where $\beta_1 = 9.00(4) \times 10^{-4}$ J/K$^2$ mol Cu, $\beta_2 = -4.87(4) \times 10^{-7}$ J/K$^6$ mol Cu. This $\beta_1$ value gives a Debye temperature of 243 K. The entropy is given by $S = f(C/T)dT$, so the shaded area in Fig. 3(a) surrounded by $C_1/T$ and $C_1/T$ corresponds to the entropy change owing to the AF ordering. The magnetic specific heat and the entropy were thus estimated, as shown in Fig. 3(b). The entropy gained below the Néel temperature is only 30% of the saturation value of 1.56(1) J/K mol Cu, reflecting the 2D nature of the system. It is known that the $S_{\text{total}} = \frac{1}{2}$ ground state of an equilateral triangle cluster is fourfold degenerate, that is, there are two degenerate Kramers doublets. In that case, the entropy change owing to the AF ordering is expected to be $(1/3)R \ln 4$ (J/K mol Cu). If the degeneracy is lifted because of the structural distortion mentioned earlier, the entropy change should be $(1/3)R \ln 2$ (J/K mol Cu). The experimen-
toral value of 1.56(1) J/K mol Cu is considerably small, even smaller than (1/3)k_B ln 2. This is probably due to an overestimation of the lattice contribution, but the number could be indicative of a reduced ordered moment. For detailed analysis of the specific heat data, it is necessary to obtain a non-magnetic isomorph and determine exact lattice specific heat. The specific heat data collected up to 100 K did not show any anomalous feature corresponding to the excitation to the higher S=5/2 states. The excitation might be screened by the large lattice specific heat or the separation was even larger. As stated already, attempts to estimate the separation between the two Kramers doublets, \([E_\Delta = J_1^2 + J_2^2 + J_3^2 - J_1 J_2 - J_2 J_3 - J_3 J_1]^{[5]}\) by fitting the susceptibility data were not successful. The calculated susceptibility did not change significantly even when \(J_1, J_2, J_3\) were taken as 50 K, indicating that the degeneracy of the two Kramers doublets with \(S=5/2\) is lifted by a slight distortion of the triangle. An external magnetic field of 20 T induced a transition from the AF state to the spin-flipped state with a saturation moment of 1\(\mu_B\) per trimer.

In conclusion, the magnetism of a 2D \(S=1/2\) trimer antiferromagnet \(La_4Cu_3MoO_{12}\) was investigated. The paramagnetic moment decreased to \(S=1/2\) per trimer \((S_{total}=1/2)\) below 250 K because of strong intratramer AF interactions. The moments localized on the trimers order antiferromagnetically at 2.6 K. The entropy change owing to the ordering is close to \((1/3)R \ln 2\ (J/K \text{ mol Cu})\), indicating that the degeneracy of the two Kramers doublets with \(S_{total}=1/2\) is lifted by a slight distortion of the triangle. An external magnetic field of 20 T induced a transition from the AF state to the spin-flipped state with a saturation moment of 1\(\mu_B\) per trimer.

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