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

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Antiferromagnetic ordering of $S = \frac{3}{2}$ triangles in La$_4$Cu$_3$MoO$_{12}$


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Magnetic properties of a cupric triangular clusters compound La$_4$Cu$_3$MoO$_{12}$ were investigated. Susceptibility data show that paramagnetic cupric spin ($S = \frac{3}{2}$) 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 35 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 $S = \frac{3}{2}$ alternating bond chains, $S = \frac{1}{2}$ two-leg ladders, and $S = \frac{1}{2}$ 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$_6$(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$_2$Cu$_3$O$_4$ (three-leg ladder) 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. $[\text{Cr}_2O\text{(CH}_3\text{COO})_6\text{(H}_2\text{O})_3]\text{Cl} \cdot 6\text{H}_2\text{O}$ and $[\text{Fe}_2O\text{(CH}_3\text{COO})_6\text{(H}_2\text{O})_3]\text{Cl} \cdot 6\text{H}_2\text{O}$ (Ref. 12) comprise almost isolated triangular clusters with isotropic spins of $S = \frac{3}{2}$ and $\frac{1}{2}$, respectively, where strong intratrimer 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. 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 nonmagnetic 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 ($S = \frac{3}{2}$) 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

![FIG. 1. Cu$_3$MoO$_4$ plane of La$_4$Cu$_3$MoO$_{12}$. The numbers show the crystallographic sites. The solid lines represent the triangle clusters.](Image)
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 PPMS 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 \( \Theta \) 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 intratrimer AF interactions give the large Weiss constant at high temperatures. The intertrimer 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 \( H = J_{1} S_{1} S_{2} + J_{2} S_{2} S_{3} + J_{3} S_{3} S_{1} + g \mu_{B} H(S_{1} + S_{2} + S_{3}) \) 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 intertrimer 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 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 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 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 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.

**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>
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</tbody>
</table>
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We propose the following picture for the present compound. Above 400 K, the susceptibility could be explained assuming $S = \frac{1}{2}$ spin localized on each Cu ion. The large AF interactions within the triangles led to a large Weiss temperature of $-558$ K. With decreasing the temperature, the Curie constant decreased to about $\frac{1}{2}$ of the high-temperature value because only the ground state with $S_{\text{total}} = \frac{1}{2}$ per cluster was populated. Since the intertriangle interactions are weak, the Weiss temperature is as small as $-16$ K. The $S_{\text{total}} = \frac{1}{2}$ spins localized on the trimers order antiferromagnetically at $2.6$ K.

In conclusion, the magnetism of a 2D $S = \frac{1}{2}$ trimer antiferromagnet Lu$_4$Cu$_3$MoO$_{12}$ was investigated. The paramagnetic moment decreased to $S = \frac{1}{2}$ per trimer ($S_{\text{total}} = \frac{1}{2}$) 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 mol Cu), indicating that the degeneracy of the two Kramers doublets with $S_{\text{total}} = \frac{1}{2}$ 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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![Magnetization curve of La$_4$Cu$_3$MoO$_{12}$ measured in pulsed magnetic field at 1.3, 4.2, and 10 K.](image)