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Antiferromagnetic ordering of $S=\frac{1}{2}$ triangles in $La_4Cu_3MoO_{12}$

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Magnetic properties of a cupric triangular cluster compound $La_4Cu_3MoO_{12}$ 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,[1] $S=\frac{1}{2}$ two-leg ladders,[2] and $S=1$ chains (Haldane systems).[3] The discovery of inorganic model compounds such as $CuGeO_3$ (spin-Peierls),[4] $(VO)_2P_2O_7$ (alternating chain),[5] Y_2BaNiO_5 (Haldane),[6] $SrCu_2O_3$,[7,8] and $Sr_{14}Cu_{24}O_{41}$[9] (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 CaV_4O_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. $Sr_2Cu_3O_5$ (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. $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$ and $[Fe_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$ (Ref. 12) comprise almost isolated triangular clusters with isotropic spins of $S=\frac{3}{2}$ and $\frac{5}{2}$, respectively, where strong intratrimer AF interactions make the multiplet with $S_{total}=\frac{1}{2}$ 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.

$La_4Cu_3MoO_{12}$ is a layered compound with an average structure of the $YAlO_3$ type.[14] The Cu_3MoO_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^{6+} ions. One can consider the Cu_3MoO_4 layer as being made of Cu_3O 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_3MoO_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 $S_{total}=\frac{1}{2}$ 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_2O_3, CuO, and MoO_3. These were mixed in appropriate ratios, pressed into a pellet, heated at 1025 °C in air for 4

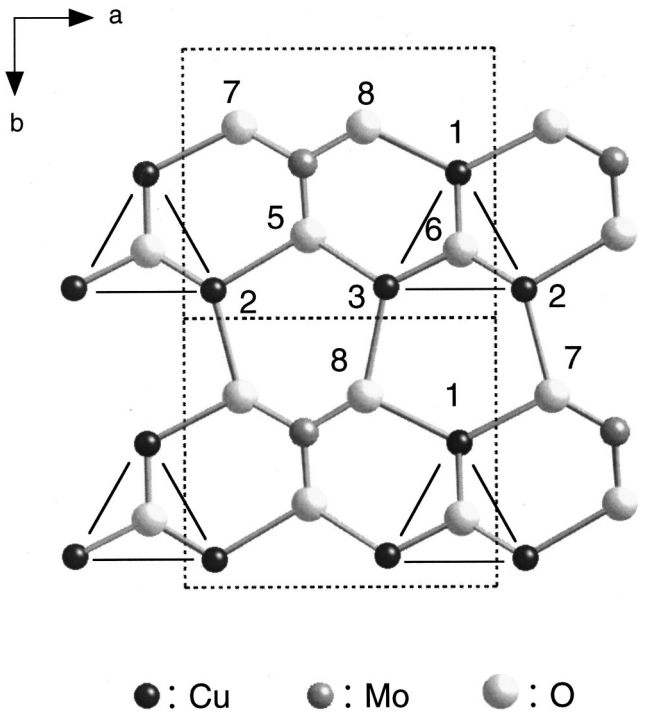

FIG. 1. Cu_3MoO_4 plane of $La_4Cu_3MoO_{12}$. The numbers show the crystallographic sites. The solid lines represent the triangle clusters.

TABLE I. Selected bond lengths and angles for $La_4Cu_3MoO_{12}$.

Atoms	Bond length (Å)	Atoms	Bond angle (deg)
intratriangle			
Cu1-O6	1.927	Cu1-O6-Cu2	123.61
Cu2-O6	1.916	Cu2-O6-Cu3	121.11
Cu3-O6	2.106	Cu3-O6-Cu1	115.28
intertriangle			
Cu1-O7	2.643	Cu1-O7-Cu2	102.48
Cu2-O7	2.800		
Cu1-O8	2.675	Cu1-O8-Cu3	105.05
Cu3-O8	2.842		
Cu2-O5	2.780	Cu2-O5-Cu3	116.55
Cu3-O5	2.399		

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 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 $H=J_1\mathbf{S}_1\mathbf{S}_2+J_2\mathbf{S}_2\mathbf{S}_3+J_3\mathbf{S}_3\mathbf{S}_1+g\mu_B\mathbf{H}(\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3)$ 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

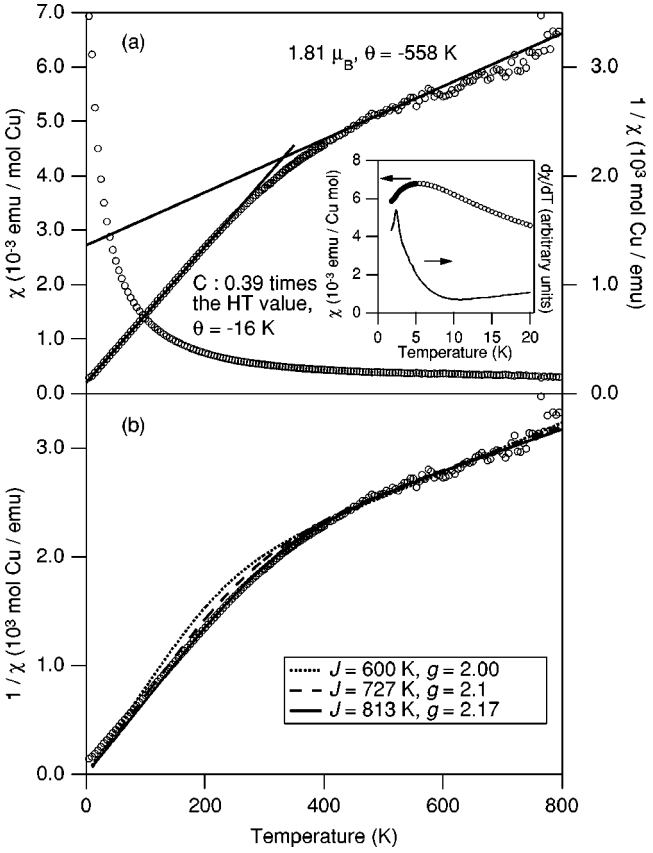

FIG. 2. (a) Temperature dependence of the magnetic susceptibility of $La_4Cu_3MoO_{12}$ below 800 K. The solid lines correspond the fit to the Curie-Weiss law. The inset shows the data taken at 0.1 T. (b) Result of the fitting to the isolated equilateral triangle model.

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 λ-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 $C_l=\beta_1T^3+\beta_2T^5$, where $\beta_1=9.00(4)\times10^{-4}$ J/K^4 mol Cu, $\beta_2=-4.87(4)\times10^{-7}$ J/K^6 mol Cu. This β_1 value gives a Debye temperature of 243 K. The entropy is given by $S=\int(C/T)dT$, so the shaded area in Fig. 3(a) surrounded by C_p/T and C_l/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 $(1/3)R\ln4$ (J/K mol Cu). If the degeneracy is lifted because of the structural distortion mentioned earlier, the entropy change should be $(1/3)R\ln2$ (J/K mol Cu). The experimen-

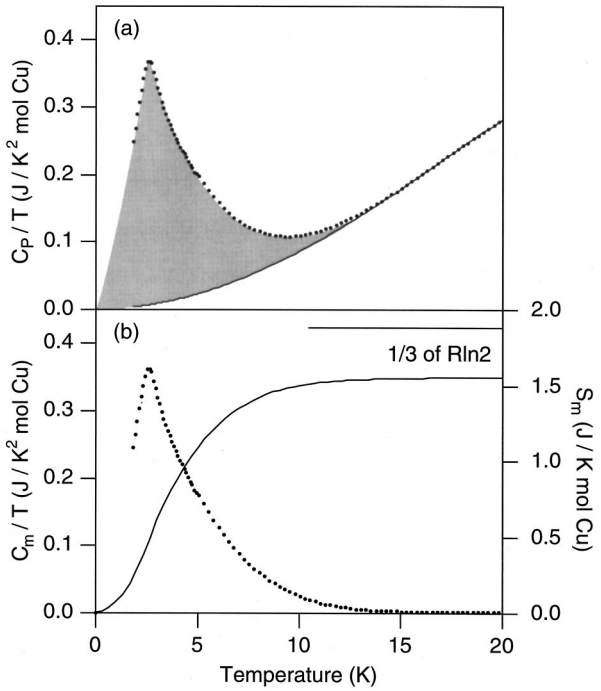

FIG. 3. (a) Total specific heat divided by temperature C_p/T vs T. The solid line stands for the lattice contribution. The magnetic specific heat divided by temperature (C_m/T, dots) and the magnetic entropy (solid line) are plotted in (b).

tal value of 1.56(1) J/K mol Cu is considerably small, even smaller than $(1/3)R\ln 2$. 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 nonmagnetic 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 $S_{\text{total}}=\frac{1}{2}$ 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, $[E_\Delta=(J_1^2+J_2^2+J_3^2-J_1J_2-J_2J_3-J_3J_1)^{0.5}]$ by fitting the susceptibility data were not successful. The calculated susceptibility did not change significantly even when $J_i-J_j=50$ K, like $J_1=J_2=796$ K, $J_3=846$ K ($E_\Delta=50$ K) and $J_1=766$ K, $J_2=816$ K and $J_3=866$ K ($E_\Delta=87$ K), for example. Inelastic neutron scattering is necessary to study the excitation spectrum of this system in more detail.

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 $\frac{1}{3}$ 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

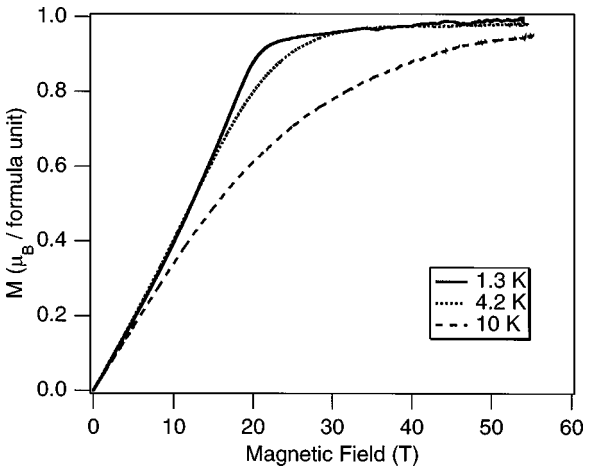

FIG. 4. Magnetization curve of $La_4Cu_3MoO_{12}$ measured in pulsed magnetic field at 1.3, 4.2, and 10 K.

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.

If intertriangle interactions are weak, it should be possible to align the ordered spins by applying magnetic field (spin flip). The results of the magnetization measurements at 1.3, 4.2, and 10 K are shown in Fig. 4. At 1.3 K, the data below 20 T were concave, reflecting the AF ordering, whereas above 20 T the magnetization tended to saturate at $1\mu_B$ / formula unit, i.e., $1\mu_B$ per trimer. This confirms that the system orders antiferromagnetically, keeping the nature of the ground state with $S_{\text{total}}=\frac{1}{2}$. The full magnetization of this system should be $3\mu_B$ / formula unit, so the observed saturationlike behavior is actually an intermediate plateau. The excitation energy from the $S_{\text{total}}=\frac{1}{2}$ to $S_{\text{total}}=\frac{3}{2}$ state is $1.5J$ for an equilateral triangle. Applying $J=813$ K, estimated from the susceptibility data, it is expected that another spin flip will be observed at 1500 T. The data at 4.2 K and 10 K also tended to saturate at the same value, $1\mu_B$ / formula unit. This is consistent with the susceptibility data which obeyed the Curie Weiss law with $S_{\text{total}}=\frac{1}{2}$ below 250 K.

In conclusion, the magnetism of a 2D $S=\frac{1}{2}$ trimer antiferromagnet $La_4Cu_3MoO_{12}$ 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 intratrimer 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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