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LETTER TO THE EDITOR

The spin gap in a quantum antiferromagnet on the kagomé lattice

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Abstract

A new spin $S = \frac{1}{2}$ antiferromagnet on the kagomé lattice, $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ (titmb = 1, 3, 5-tris(imidazol-1-ylmethyl)-2, 4, 6 trimethylbenzene), has been grown and its magnetic properties have been studied. We have found for the first time a two-peak feature in the temperature dependence of the heat capacity. The higher-temperature peak is explained as due to a short-range magnetic ordering in two dimensions. We analysed the lower-temperature peak on the basis of an energy level scheme with a singlet ground state and a spin gap to the first excited triplet. The analysis reproduces the experiment fairly well, suggesting that the ground state is a disordered quantum liquid.

The kagomé lattice consists of a repeated pattern of a hexagon and the six triangles attached around it as shown in figure 1. When magnetic moments are placed at the vertices of the kagomé lattice, a fascinating property results if the interaction among the moments is antiferromagnetic. For large spin quantum numbers ($S \gg \frac{1}{2}$), the moments in a triangle of the kagomé lattice cannot accommodate an antiparallel arrangement due to the so-called geometrical frustration and make the angle 120° with each other in the ground state. For an $S = \frac{1}{2}$ antiferromagnet on the kagomé lattice, theories predict that the ground state is a disordered quantum liquid with a spin gap to the excited states [1–3]. The ground state of an $S = \frac{1}{2}$ kagomé Heisenberg antiferromagnet (KHA) may be described by a quantum dimer mode [4].

The antiferromagnetic materials having the kagomé structure studied so far are $SrGa_4Cr_8O_{19}$ [5–7], jarosites [8–10], m-N-methylpyridinium α-nitronyl nitroxide [11], $Ba_2Sn_2Ga_3ZnCr_7O_{22}$ [12], and volborthite [13]. In all of these materials except the last one, the spin quantum numbers are larger than 1. In this letter, we study a new $S = \frac{1}{2}$ KHA, $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ (titmb = 1, 3, 5-tris(imidazol-1-ylmethyl)-2, 4, 6 trimethylbenzene) in which Cu^{2+} has $S = \frac{1}{2}$. The anisotropy in the g-tensor is small [14], so the Heisenberg model can be applied for the exchange interaction among the moments.

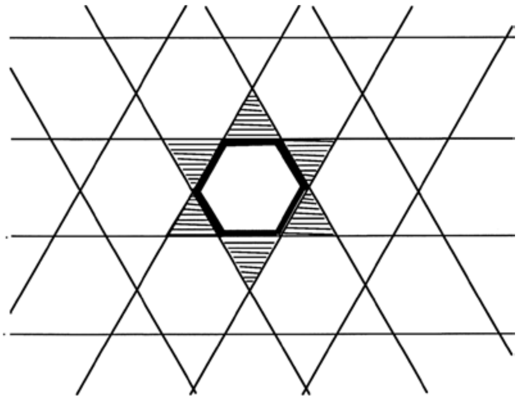

Figure 1. A kagomé lattice consisting of a repeated pattern of a hexagon and the six triangles attached around it.

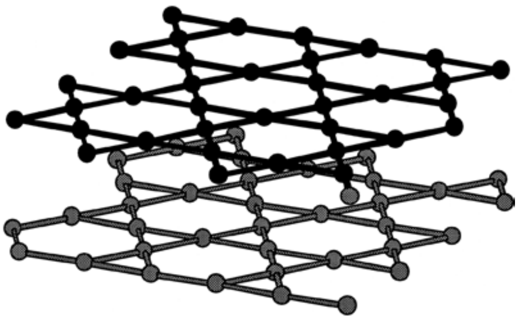

Figure 2. The crystal structure of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. Only Cu atoms are shown for clarity.

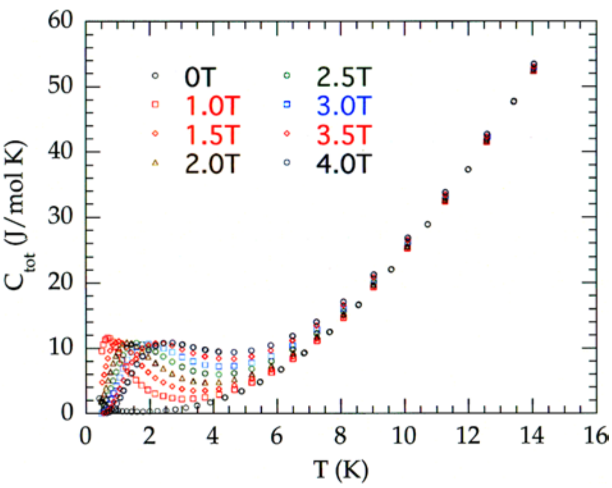

Figure 3. The temperature dependence of the total heat capacity of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ in zero and applied magnetic fields.

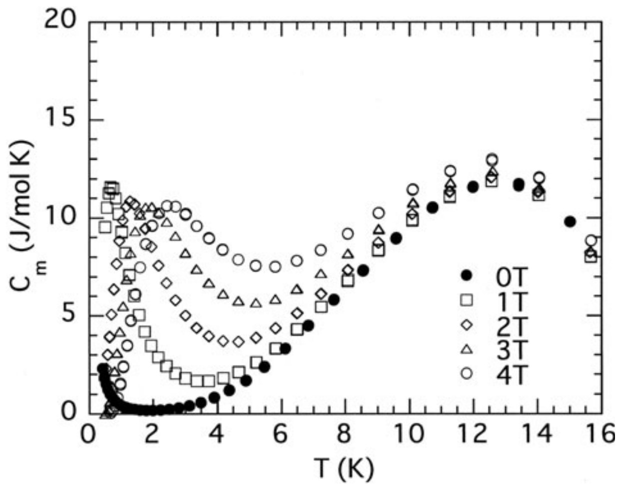

Figure 4. The temperature dependence of the magnetic part of the heat capacity in $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ after subtracting the lattice heat capacity.

The crystal structure of this material is shown in figure 2. In this figure only Cu atoms are shown for clarity and one sees two layers of kagomé lattices. Large molecules are present between the layers and so the exchange interaction between the layers is expected to be much smaller than that within a layer.

Powder samples of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ were grown by the method described in [14]. The material, 1, 3, 5-tris(imidazol-1-ylmethyl)-2, 4, 6-trimethylbenzene, was purchased from the Wako Pure Chemical Industries, Ltd. Heat capacity data were taken with a Quantum Design PPMS.

Figure 3 shows the measured heat capacity, C_{tot}, including the contribution of the lattice, as a function of temperature for the designated magnetic fields. In zero field, C_{tot} deceases with decreasing temperature and shows an upturn below 1 K. With the application of an external magnetic field, H, a peak appears whose position moves to the high-temperature side with increasing H. Also the peak width becomes broader as H is increased. In order to get the magnetic part of the heat capacity, C_{m}, we have subtracted the lattice heat capacity, C_{lattice}, from C_{tot} assuming that C_{lattice} varies with temperature, T, as $C_{\mathrm{lattice}} = aT^3$, with $a = 0.0149$ J mol^{-1} K^{-4}. The temperature dependence of C_{m} thus obtained is shown in figure 4. In this figure we see a broad peak at about 13 K in addition to the low-temperature peak already seen in the raw data. This broad peak reflects the entropy change associated with a short-range magnetic ordering in low dimensions [15]. We integrated C_{m} over T to get the magnetic entropy. The inset of figure 5 shows the temperature dependence of the magnetic entropy. The entropy acquires the value $\simeq Nk_{\mathrm{B}} \ln 2$ at high temperatures expected for an $S = \frac{1}{2}$ magnet, where N is the total number of magnetic atoms in the system and k_{B} is the Boltzmann constant. This result shows that our estimate of the lattice heat capacity is reasonable.

The appearance of a peak in C_{m} at low temperature suggests the presence of an energy gap. We have analysed the temperature and magnetic field dependence of C_{m} on the basis of a simple energy level scheme, namely, a singlet ground state and a first excited triplet with a spin gap, Δ. After a simple calculation we have

$$C_{\mathrm{m}} = -\beta \frac{N}{T}\left(\frac{\mathcal{A}}{(1 + \mathrm{e}^{-\beta\Delta} + \mathrm{e}^{-\beta(\Delta+\varepsilon)} + \mathrm{e}^{-\beta(\Delta-\varepsilon)})^2}\right), \qquad (1)$$

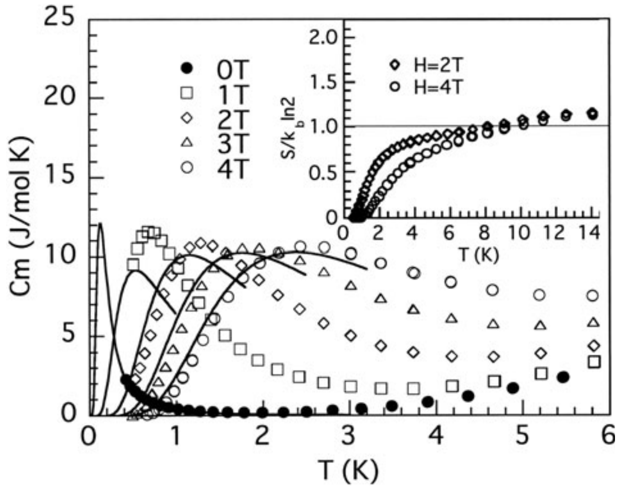

Figure 5. The result of the analysis discussed in the text is compared with the experiment. Inset: the temperature dependence of the magnetic entropy in $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$.

where

$$\beta \equiv \frac{1}{k_B T}, \tag{2}$$

$$\epsilon \equiv g\mu_B H, \tag{3}$$

and

$$\begin{aligned}\mathcal{A} \equiv (&-\Delta^2 e^{-\beta\Delta} - (\Delta+\varepsilon)^2 e^{-\beta(\Delta+\varepsilon)} - (\Delta-\varepsilon)^2 e^{-\beta(\Delta-\varepsilon)})(1 + e^{-\beta\Delta} + e^{-\beta(\Delta+\varepsilon)} + e^{-\beta(\Delta-\varepsilon)}) \\ &- (\Delta e^{-\beta\Delta} + (\Delta+\varepsilon)e^{-\beta(\Delta+\varepsilon)} + (\Delta-\varepsilon)e^{-\beta(\Delta-\varepsilon)}) \\ &\times (-\Delta e^{-\beta\Delta} - (\Delta+\varepsilon)e^{-\beta(\Delta+\varepsilon)} - (\Delta-\varepsilon)e^{-\beta(\Delta-\varepsilon)}).\end{aligned} \tag{4}$$

The result of the analysis is shown in the main panel of figure 5. We were able to reproduce the experiment rather nicely with $\Delta/k_B = 0.37$ K and $g = 2.20$. The g-value obtained in this study is consistent with that reported before [14]. Theory predicts that there are many non-magnetic states between the singlet ground state and the lowest excited triplet [2]. We have tried to analyse our data by introducing a singlet state located at Δ' ($0 < \Delta' < \Delta$). Although the position of the peak in C_m is better reproduced, the calculated peak height is larger than the experimental value.

By comparing the position of the high-temperature peak in C_m with the results of the numerical calculations [16, 17], we obtain the value $J/k_B \approx 19$ K for the nearest-neighbour exchange interaction. From the numerical calculation [2], the lower bound is set to $\Delta \approx J/20$ for the spin gap. In the present case, this gives $\Delta/k_B \approx 1$ K, which is larger than that obtained experimentally ($\Delta/k_B = 0.37$ K). Further theoretical studies seem to be necessary.

The two-peak feature in the temperature dependence of heat capacity has been reported in ^{3}He adsorbed on a graphite substrate [18, 19] and has been analysed by an $S = \frac{1}{2}$ KHA model [20]. It turns out that the interaction between ^{3}He nuclear spins is more complex than originally thought and one needs multiple-spin exchange interactions to explain the behaviour [21]. We believe, therefore, that this is the first observation of a two-peak feature in the heat capacity of an $S = \frac{1}{2}$ KHA. The observation of the lower-temperature peak gives evidence for the existence of a spin gap in this quantum antiferromagnet.

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