Observation of a Transient Magnetization Plateau in a Quantum Antiferromagnet on the Kagomé Lattice

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Abstract. – The magnetization process of an \( S = \frac{1}{2} \) antiferromagnet on the kagomé lattice, \([\text{Cu}_3\text{(titmb)}_2(\text{OCOCH}_3)_6] \cdot \text{H}_2\text{O}\) (titmb= 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6 trimethylbenzene) has been measured at very low temperatures in both pulsed and steady fields. We have found a new dynamical behavior in the magnetization process. A plateau at one third of the saturation magnetization \( M_s \) appears in the pulsed field experiments for intermediate sweep rates of the magnetic field and disappears in the steady field experiments. A theoretical analysis using exact diagonalization yields, \( J_1 = -19 \pm 2K \) and \( J_2 = 6 \pm 2K \), for the nearest neighbor and second nearest neighbor interactions, respectively. This set of exchange parameters explains the very low saturation field and the absence of the plateau in the thermodynamic equilibrium as well as the two-peak feature in the magnetic heat capacity observed by Honda et al. [Z. Honda et al., J. Phys.: Condens. Matter 14, L625 (2002)]. Supported by numerical results we argue that a dynamical order by disorder phenomenon could explain the transient appearance of the \( M_s/3 \) plateau in pulsed field experiments.

The study of quantum phenomena in magnetic systems has been a central subject in condensed matter research in recent years. Lower dimensional antiferromagnets show many interesting phenomena originating from quantum fluctuations. One of the examples of these phenomena is the appearance of a singlet ground state and a spin gap to the excited triplet in a spin, \( S=1 \) one-dimensional Heisenberg antiferromagnet (1D HAF) [1], a spin-Peierls system [2] and an \( S=\frac{1}{2} \) two-leg spin ladder [3]. Another interesting example is the appearance of a magnetization plateau, a phenomenon in which the magnetization, \( M \), of an antiferromagnet stays constant in a finite range of applied magnetic fields, \( B \), before reaching the saturated phase. In the last few years, magnetization plateaus have been observed in several quantum antiferromagnets including an \( S=1 \) 1D antiferromagnet with bond alternation [4], the coupled dimer

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compound NH$_4$CuCl$_3$ [5] and SrCu$_2$(BO$_3$)$_2$ [6–11]. The origin of the magnetization plateau in these quantum antiferromagnets differs for different compounds since a magnetization plateau can be expected to occur from various combinations of dimensionality and frustration of interactions [12]. Theory predicted that a quantum antiferromagnet on the kagomé lattice with a nearest neighbor Heisenberg interaction, which is a typical example of frustrated magnets, would also show a magnetization plateau at one third of the saturation magnetization $M_s$ [12–14]. There has been, however, no experimental finding of the magnetization plateau in kagomé antiferromagnets. In this paper, we report the first observation of a magnetization plateau in the $S=\frac{1}{2}$ kagomé antiferromagnet, [Cu$_3$(titmb)$_2$(OCOCH$_3$)$_6$]$\cdot$H$_2$O, (titmb=1,3,5-tris(imidazol-1-ylmethyl)-2,4,6 trimethylbenzene) (hereafter, abbreviated to Cu-titmb).

First, we summarize the crystal and magnetic properties of Cu-titmb. The crystal structure of this material has been determined by Liu et al. [15] and is shown schematically in Fig. 1. As is seen from Fig. 1(a), Cu$^{2+}$ ions are placed at the vertices of the triangles. The distance between the Cu$^{2+}$ ions on a triangle is 7.77 Å. These triangles are attached to a hexagon. A two dimensional array of such pattern is called the kagomé lattice. The kagomé layers are stacked along the c axis as shown in Fig. 1(b) with the inter layer distance of 7.05 Å. We define the nearest neighbor exchange interaction, $J_1$, between Cu$^{2+}$ spins in a kagomé layer as the one along the edges of a triangle through H$_2$O and/or CH$_3$COO$^-$. The former path is expected to dominate because the latter path is connected by a weak hydrogen bond. The second neighbor interaction, $J_2$, is defined as the one between a spin and the spins on the second neighboring vertices of the hexagon. Since no apparent exchange paths exist between spins on the adjacent kagomé layers along the c axis, the interaction between layers is expected to be much smaller than $J_1$ and $J_2$.

Heat capacity measurements were performed on a powder sample of Cu-titmb [16]. The magnetic heat capacity, $C_m$, obtained after subtraction of the lattice heat capacity is shown in the inset of Fig. 2 as a function of temperature, $T$. We see a two peak structure which is a feature predicted for an $S=\frac{1}{2}$ antiferromagnet on the kagomé lattice with the nearest neighbor Heisenberg interaction [17–19] and for other frustrated quantum magnets [12].

Powder samples of Cu-titmb were grown by the method described in [15]. The material, 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene, was purchased from the Wako Pure Chemical Industries, Ltd. The magnetization measurements were performed at Osaka University under pulsed high fields in conjunction with a dilution refrigerator. Pulsed magnetic fields are generated by discharging the energy stored in a capacitor bank through the coil. The duration time of the pulsed field is given roughly by $(LC)^{\frac{1}{2}}$, where $L$ is the inductance of the coil and $C$ is the capacitance of the bank. Since the magnetic field changes sinusoidally with time, the field sweep rate, $dB/dt$, differs for different field values. In the following, we denote the field sweep rate as the one obtained at around 1.5 T. To change the sweep rate, we have to change either, $C$, $L$ and/or the peak field. In this experiment, we used two sets of capacitor banks and were able to measure the magnetization over a wide range of sweep rates. However, we were not able to access the sweep rates below 0.7 T/msec and those between 1.9 T/msec and 14 T/msec from the technical reason described above. The powder sample was packed into a Teflon tube and immersed in the mixing chamber of the dilution refrigerator. In the pulsed field measurements, we observe the derivative of magnetization with respect to time, $dM/dt$. Simultaneously, we measure the time evolution of $B$. Combining these two sets of data, we get $M$ vs $B$ curve. Figure 2 shows the magnetization as a function of applied magnetic field measured at 100 mK in increasing and decreasing fields. We see a magnetization plateau at $M_s/3$ for $0.5 \leq B \leq 2.5$ T in the increasing field run. Then the magnetization increases almost linearly with increasing field up to saturation. The magnetization becomes saturated above about 10 T with the saturation moment of about 1 $\mu_B$ per Cu atom. This
value of $M_s$ is consistent with the value expected for a Cu$^{2+}$ with $S = \frac{1}{2}$ and $g = 2.20$ [15]. Surprisingly, no plateau has been observed in decreasing field. Figure 3 shows the magnetization curve measured in increasing fields with different sweep rates. As the field is swept slower, the $M_s/3$ plateau becomes less pronounced. When $B$ is swept much faster, we do not see the plateau either. The results presented in Figs. 2 and 3 suggest that the $M_s/3$ plateau might be metastable. In order to get a magnetization curve in equilibrium, we have measured the magnetization of Cu-titmb by the Faraday method in steady fields using a superconducting magnet [20]. A powder sample of Cu-titmb was mixed with Apiezon-N grease and put on one of the plates of the capacitor. In order to ensure a good thermometry, Cu foils were used to link the sample and the mixing chamber. Figure 4 shows the results. In the thermodynamic limit, the magnetization increases abruptly with increasing fields from almost zero and no plateau is seen. Saturation of the magnetization is observed at $B_{\text{sat}} \sim 0.2$ T.

In the following, we discuss theoretically the experimental results reported above. The proximity of a ferromagnetic instability due to a competition between ferromagnetic and antiferromagnetic exchange interactions is the simplest explanation for the anomalously low saturation field, $B_{\text{sat}}$, measured in the static experiments. Such competing interactions may be described by a $J_1 - J_2$ model on the kagomé lattice, with $J_1 \times J_2 < 0$. The model reads:

$$\mathcal{H} = J_1 \sum_{<i,j>} S_i S_j + J_2 \sum_{<<i,k>>} S_i S_k$$

(1)

where the first and second sums run on the first and second neighbors respectively. For pure antiferromagnetic $J_1$ (or $J_2$) couplings and in a finite range of parameters around these situations the system is in the special spin liquid phase which has been the subject of many studies [17,18,21]. A large enough second neighbor ferromagnetic interaction drives the system towards the so-called $\sqrt{3} \times \sqrt{3}$ three-sublattice Néel order, whereas a combination of antiferromagnetic $J_1$ and $J_2$ induces a $q = 0$ three-sublattice Néel order [22]. A ferromagnetic phase exists over a large range of $J_1$ and $J_2$, which become unstable when the antiferromagnetic second-neighbor interaction becomes large ($J_2/J_1 > -0.35$). As will be explained below, we found that Cu-titmb is in this range of parameters very close to the ferromagnetic phase. For these coupling parameters a numerical calculation up to 36 sites gives the quantum eigen-spectra which show a 12 sublattice Néel order with a non coplanar order parameter, in agreement with the classical solution. A spin wave calculation remains to be done to give a plausible estimate of the reduction of the order parameter by long-wave-length quantum fluctuations [23]. In the experiments $B_{\text{sat}}$ is very low compared to $T_{\text{max}}$, the temperature at which $C_m$ shows a broad peak (see Fig. 2): the dimensionless parameter, $\theta = (g\mu_B B_{\text{sat}})/(k_B T_{\text{max}})$ is approximately 0.02, whereas this ratio is expected to be of the order of one in an unfrustrated antiferromagnet and is 4.5 in the pure antiferromagnetic model on the kagomé lattice [12–14,17]. In the $J_1 - J_2$ model, $\theta$ decreases when approaching the boundary of the ferromagnetic phase [23]. A value of $\theta$ consistent with the experimental one is obtained in the vicinity of the ferromagnetic instability either with ferromagnetic $J_1$ and antiferromagnetic $J_2$ with $J_2/J_1 \sim -0.3$, or with antiferromagnetic $J_1$ and ferromagnetic $J_2$ with $J_2/J_1 \sim -50$. Mizuno et al. [24] have calculated the exchange interactions in copper oxides. They showed that the exchange interaction between Cu$^{2+}$ spins through an oxygen atom is ferromagnetic when the bond angle is around 90°. We, therefore, adopt a ferromagnetic $J_1$.

A reasonable agreement between the experimental data for $T_{\text{max}}$ and $B_{\text{sat}}$ is obtained with $J_1 = -19 \pm 2 K$ and $J_2 = 6 \pm 2 K$. This set of $J_1$ and $J_2$ also predicts a double peak feature in $C_m$ as observed experimentally (Fig. 2). At the thermodynamic limit, this model has no magnetization plateau as will be shown below.
Such a competition of interactions induces a very high density of low lying magnetic states. Numerous magnetic excitations are thus at very low energy and very small perturbations can change the magnetic behavior. We have observed in our numerical study a general phenomenon that might be relevant to the real physical behavior of the compound. Samples with \( N = 21 \) and 27 which do not accommodate the wave vectors at \((0, \pi), (\pi, 0)\) or \((\pi, \pi)\) in their Brillouin zone frustrate the thermodynamic ground state and display a \( \frac{1}{3} \) plateau as shown in Fig. 5. In this figure, is shown the dependence of the field range, \( B_2 - B_1 \), at which the magnetization plateau at \( m(= M/M_s) = \frac{1}{3} \) appears on the energy per spin, \( e(m) \), in this state. At the thermodynamic limit shown schematically in the inset, a cusp in the \( e(m) \) curve at \( m=m_0 \) is the signature of a \( m_0 \) magnetization plateau bounded by the two fields \( B_1 \) and \( B_2 \) which measure the slopes of the \( e(m) \) curve on the left and right of \( m_0 \) [12]. Exact diagonalization on finite size samples gives the energy per spin versus magnetization for the discrete values \( m=2S_{\text{tot}}/N \). These energies are then fitted to two polynomial forms allowing an eventual discontinuity of the slopes at the specific point \( m_0 \). The best fits are obtained with a discontinuity at \( m = \frac{1}{4} \) and give the width \( B_2 - B_1 \) of the magnetization plateau reported in the figure. The error bars represent the uncertainties in the parameters of each fit. The results for the sizes multiples of 6 (\( N=18, 24, 30 \) and 36) exhibit zero width (i.e. no plateau) in the thermodynamic limit. The \( N=21 \) and 27 samples, which do not allow the wave vectors \((0, \pi), (\pi, 0), (\pi, \pi)\) have a higher energy per spin and exhibit a plateau at \( m = \frac{1}{4} \). At any magnetization the energy per spin of these samples at \( T=0 \) is indeed slightly higher than the true thermodynamic ground-state and thus the system is in a metastable configuration. At \( M_s/3 \), this metastable state is associated with an up-up-down \((uud)\) configuration of spins, where spins along the horizontal lines in Fig. 1(a) are ferromagnetically aligned in the up direction, whereas the extra spins of the triangles are down [12]. Three such configurations are possible and thus we have three domains.

Among all the configurations of spins that are at very low energy at \( M_s/3 \), purely geometric arguments imply that the three \( uud \) configurations have in phase space the largest attraction basin for fluctuations, either thermal or quantum, and thus a lock-in of the system in such configurations can be driven by a large number of very small perturbations. This is a transient analogue of the phenomenon of order by disorder [25–27]. In such a scenario there exist in the free energy landscape three large metastable wells associated with the three possible \( uud \) configurations. Two characteristic times of the out of equilibrium dynamics in such a landscape are then of importance: the relaxation time, \( \tau_r \), which is dominated by the curvature of the metastable well, and the Kramers escape time from the well, \( \tau_{\text{esc}} \), which involves both the characteristics of the well and of the surrounding energy barriers. If the sweep rate, \( \Gamma \), of the magnetic field is larger than \( \tau_r^{-1} \) no signature of the metastable well can be seen. If \( \Gamma \) is smaller than \( \tau_{\text{esc}}^{-1} \), the system relaxes to the equilibrium situation and no magnetization plateau is observed. For sweep rates \( \tau_{\text{esc}}^{-1} < \Gamma < \tau_r^{-1} \), the system can stay for a while in the metastable well and display a \( M_s/3 \) plateau. Such a picture of the dynamics should be supported by a stochastic description of the evolution of a small cluster of spins with a Fokker Planck equation. In such an approach typically \( \tau_r = \gamma/\omega_0^2 \) where \( \omega_0 \) is the smallest spin wave pulsation in the metastable configuration and \( \gamma \) is a phenomenological friction coefficient. Whatever the origin of the escape from the metastable well, \( \tau_{\text{esc}} \) is noticeably larger than \( \tau_r \); it involves a factor which depends exponentially on the height, \( \Delta \) of the potential energy barrier. In the classical regime typically \( \ln(\tau_{\text{esc}}) \) is proportional to \( \Delta/(\chi \gamma D) \), where \( \chi \) is the homogeneous susceptibility of the cluster and \( D \) the spin diffusion coefficient. In the quantum tunnelling regime, which is more probable in the present case, \( \ln(\tau_{\text{esc}}) \propto \sqrt[3]{\Delta \chi} \). More theoretical and experimental work is indeed needed to clarify this point.

In conclusion, we have measured the magnetization process of the \( S = \frac{1}{2} \) antiferromagnet
on the kagomé lattice, Cu-titmb, at very low temperatures in both pulsed and steady fields. We have found for the first time a $M_s/3$ plateau in a certain range of field sweep rates in the pulsed field measurements. A theoretical analysis using exact diagonalization yields, $J_1 = -19 \pm 2K$ and $J_2 = 6 \pm 2K$, for the nearest neighbor and second nearest neighbor interactions, respectively. This set of exchange parameters also explains the two-peak feature in the magnetic heat capacity observed by Honda et al. [16]. This very strong frustration and proximity of the ferromagnetic phase is the origin of a very large density of low lying magnetic states. Amongst these states the $uud$ configurations are not very far in energy from the absolute ground state and can be selected by an effect of order by disorder. This might be an explanation of the transient appearance of a metastable plateau at $M_s/3$ with appropriate sweeping rates of the magnetic field.

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Fig. 1 – The crystal structure of $[\text{Cu}_3(\text{titmb})_2(\text{OCOCH}_3)_6]\cdot\text{H}_2\text{O}$.

Fig. 2 – The magnetization versus applied magnetic field curve of $[\text{Cu}_3(\text{titmb})_2(\text{OCOCH}_3)_6]\cdot\text{H}_2\text{O}$ measured in increasing and decreasing field runs at $T = 100$ mK. Inset: The temperature dependence of the magnetic heat capacity of $[\text{Cu}_3(\text{titmb})_2(\text{OCOCH}_3)_6]\cdot\text{H}_2\text{O}$ measured at the designated magnetic fields.

Fig. 3 – The magnetization versus applied magnetic field curve obtained in increasing field runs with the designated sweep rates at $T = 100$ mK.

Fig. 4 – The magnetization versus applied magnetic field curve obtained in a steady field at the designated temperatures.

Fig. 5 – Dependence of the field range, $B_2 - B_1$, at which the $m = \frac{1}{3}$ plateau appears on the energy per spin, $\epsilon(m)$ in this state. Inset: $\epsilon$ versus $m$ in the thermodynamic limit.
Fig. 1 Narumi et al.

(a)

(b)

- $\text{Cu}^{2+}$
- $\text{CH}_3\text{CO}_2^-$
- $\text{H}_2\text{O}$
- titmb
Fig. 2 Narumi et al.

Magnetization ($\mu_B$/Cu) vs. Magnetic Field (T) at $T = 0.1$ K.
Fig. 3 Narumi et al.
Fig. 4  Narumi et al.
Fig. 5 Narumi et al.