High-field magnetization of a two-dimensional spin frustration system, \( \text{Ni}_5(\text{TeO}_3)_4X_2 \) (X = Br, Cl)

J L Her\(^1\), Y H Matsuda\(^1\), K Suga\(^1\), K Kindo\(^1\), S Takeyama\(^1\), H Berger\(^2\) and H D Yang\(^3\)

\(^1\) Institute for Solid State Physics, University of Tokyo, Japan
\(^2\) Institutes of Physics of Complex Matter, EPFL, Lausanne, Switzerland
\(^3\) Department of Physics, Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Taiwan

Received 26 June 2009
Published 8 October 2009
Online at stacks.iop.org/JPhysCM/21/436005

Abstract
The high-field magnetization, \( M(H) \), of \( \text{Ni}_5(\text{TeO}_3)_4X_2 \) (X = Br, Cl) was measured by using a pulse magnet. These compounds have a two-dimensional crystal structure and a distorted Kagome spin frustrated system which is built from the Ni\(^{2+}\) ions (\( S = 1 \)). The Néel transition temperatures are \( T_N \approx 28 \) and 23 K for X = Br and Cl, respectively. When \( T < T_N \), we observe step-like transitions, at \( H_c \approx 11 \) and 10 T for X = Br and Cl, respectively. On the other hand, for \( T > T_N \), the field-dependent magnetization curves behave like a monotonically increasing straight line up to 55 T. The \( H_c \) value is close to those obtained in previous spin resonance studies in which a model of a spin-flop scenario was proposed to explain the field-dependent resonance spectra. With the earlier model a further transition at around 23 T was predicted; however, our observations did not show any plateau behaviors, saturation or other anomalies up to 55 T, suggesting that the further transition possibly exists in a much higher field region.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The frustration of spins coupled antiferromagnetically is an ongoing and interesting subject in condensed matter physics. The quantum spin fluctuation in such a frustrated system, which causes a large amount of degenerate ground states, interferes with the formation of a long-range Néel order. On the other hand, the magnetic anisotropy of spins can open a gap in a low-lying excitation spectrum, leading to the occurrence of long-range ordering states. The competition between magnetic anisotropy and spin frustration results in various kinds of magnetic ordering phases. A two-dimensional (2D) Kagome spin frustrated system is a remarkable one in which to study these interesting magnetic phases, due to the anisotropic nature and unique spin arrangement. Extensive studies were performed on the Kagome spin system and they discovered diverse magnetic ground states, such as a quantum liquid [1], a spin gap [2], antiferromagnetic [3] and ferromagnetic states [4] and so on.

\( \text{Ni}_5(\text{TeO}_3)_4X_2 \) (X = Br, Cl) is a new series compound with the Kagome spin system, having a well separated 2D layer structure in which the [Ni\(_5\)O\(_{17}\)X\(_2\)] units construct a 2D layer and the layers are separated by the Coulomb repulsion of the lone pairs of Te\(^{4+}\) ions [3]. The Ni\(^{2+}\) ions serve as magnetic centers with \( S = 1 \), and couple to each other through an antiferromagnetic superexchange interaction [3]. The long-range Néel ordering temperatures are 28 and 23 K for X = Br and Cl, respectively [3]. The anisotropic properties were investigated for single-crystal \( \text{Ni}_5(\text{TeO}_3)_4\)Br\(_2\), showing \( g_\parallel = 2.45 \) and \( g_\perp = 2.53 \) [5]. Recently, noncollinear arrangements of the Ni sublattices of \( \text{Ni}_5(\text{TeO}_3)_4\)Br\(_2\) were observed from neutron diffraction and magnetization measurements [6]. These studies reveal very complicated spin interactions and a unique ground state. The magnetic field effects of these compounds have been studied by means of high-field electron spin resonance (ESR) experiments, in which the antiferromagnetic resonance modes were observed on both X = Br and Cl compounds [5–8]. The observed lowest resonance mode is first softened and
then hardened by a magnetic field, having critical fields of \( \sim 10.7 \) and \( 10 \) T for \( X = \text{Br} \) and \( \text{Cl} \), respectively \([6, 9]\), suggesting that a spin-flop-like transition exists. However, the models proposed by these two reports have huge differences in handling the spin isotropic effect, where the spin anisotropy was regarded as important in one report \([6]\) but neglected in the other \([9]\). The high-field magnetization measurements can provide more information of high-field state of these samples. Very recently, Pregelj et al reported a magnetization study of \( \text{Ni}_5(\text{TeO}_3)_2\text{Br}_2 \) in magnetic fields up to 12 T. A transition peak was observed in the \( dM/dH \) curve at \( \sim 11 \) T, which is suggested to be related to the spin-flop-like transition in ESR experiments \([10]\). A model, including spin-ion anisotropy, was proposed to explain this observation. In addition, this model predicts that a second transition occurs at 23 T. It is interesting to measure the magnetization in higher fields, to confirm whether there is another transition.

In the present study, we focus on the field-dependent magnetization of these compounds using a pulse magnet which generates magnetic fields up to 55 T. A step-like transition, at around \( 11 \) T (10 T) for \( X = \text{Br} (\text{Cl}) \), was observed in the \( M(H) \) curves, which is consistent with Pregelj’s results and also with ESR experiments \([6, 9, 10]\). Interestingly, there is no signature of another field-induced transition up to 55 T. However, the \( M(H) \) curves showed unsaturated behavior up to the highest field in the current measurements, there exists the possibility of a second transition occurring at fields higher than 55 T.

2. Experiment

A plate-like single crystal was used in the measurement. The details of preparation were described in a previous report \([6]\). High-field magnetization measurements, \( M(H) \), were performed by an induction method using a pulse magnet. This system can generate pulse fields up to 55 T and the duration time is 40 ms. To obtain a stronger signal, several pieces of single crystal were used, which have total masses of \( \sim 38 \) and 17 mg for \( X = \text{Br} \) and \( \text{Cl} \), respectively. Magnetic field is applied perpendicular to the crystalline surface, i.e. the magnetic field is oriented along the \( \alpha^* \)-axis, where \( \alpha^* \) denotes the normal direction of the 2D layers. The absolute values of the magnetization curves are carefully calibrated by means of low-field magnetization measurements which were performed using a SQUID magnetometer (Quantum Design MPMS).

3. Results and discussion

Figure 1(a) shows the \( M(H) \) curve of \( \text{Ni}_5(\text{TeO}_3)_2\text{Br}_2 \) at 1.5 K. A step-like transition can be clearly seen at \( H_c \approx 11 \) T. When \( H > H_c \), the \( M(H) \) curve shows a monotonic linear increase, which shows neither saturation nor a plateau behavior up to \( H \approx 55 \) T. In figures 1(b) and (c), we show the \( M(H) \) curves at different temperatures for \( X = \text{Br} \) and \( \text{Cl} \) compounds. It is found that the two compounds show very similar behaviors. The \( M(H) \) curve at 30 K (25 K) for a Br (Cl) sample is almost a straight line which represents the paramagnetic property at \( T > T_N \). When temperatures are lower than \( T_N \), the step-like transitions start to appear at around 10 T and become more and more prominent at lower temperatures for both samples. In addition, \( M(H) \) curves for increasing and decreasing field coincide with each other without showing any hysteresis in all the cases. The \( H_c \) values are consistent with ESR results \([6, 9]\), and also the previous field-dependent magnetization data \([10]\).

In order to assist with the clarification of the transition point, we show the \( dM/dH \) curves in figure 2. At the lowest temperature, there is a sharp peak which is related to a step-like transition. This peak becomes broader with increasing temperature, and disappears at high temperatures. Although the behaviors of the two samples are quite similar, there are some differences between these two samples. First, the peak disappears just above Néel temperature for the \( X = \text{Br} \) sample. However, there remains a very weak and broad peak at \( T > T_N \) (i.e. 25 K) for the \( X = \text{Cl} \) sample. It is possibly related to some short-range ordering component which presents at \( T > T_N \). Second, in the case of \( X = \text{Cl} \), the peak positions, \( H_c \), are slightly shifted toward higher fields with increasing temperature. However, the peak positions are almost the same in the case of \( X = \text{Br} \), indicating that the temperature dependence of this transition is very weak.

The difference in magnetization between low-field and high-field states at the transition (\( \Delta M \)) can be roughly determined from the \( M(H) \) curves. In figure 3, we show a
Figure 2. $dM/dH$ curves for Ni$_5$(TeO$_3$)$_4$Br$_2$ and Ni$_5$(TeO$_3$)$_4$Cl$_2$ at some selected temperatures.

Figure 3. Typical plot for determining $\Delta M$. The red dashed line is to guide the eye. The inset shows the temperature-dependent $\Delta M$.

The typical example of an X = Br sample at 1.5 K, for which the $\Delta M$ is $\sim 1.25$ $\mu_B$/formula. The $\Delta M$ value increases with decreasing temperature and slightly decreases below 5 K (see the inset of figure 3). Interestingly, the $\Delta M$ value at the lowest temperature is nearly half of the magnetic moment of Ni$^{2+}$ ions, $m_{Ni} \sim 2.53 \mu_B$ [5], indicating that only some of the Ni$^{2+}$ ion spins participated in the transition.

According to the results of neutron and x-ray diffraction measurements, there are 20 Ni$^{2+}$ ions in a unit cell ($Z$-factor = 4). The Ni$^{2+}$ ions locate in three different crystallographic sites, in which Ni1 is in Wyckoff site 4e; Ni2 and Ni3 are in Wyckoff site 8f [3, 6]. The spin orientations depend on the Ni sites. Figure 4(a) shows a sketch of the ten sublattice spin configurations of these compounds, in which 1, 2, and 3 denote Ni1, Ni2, and Ni3 sites. We use the same notation as in the neutron scattering report [6]. It should be noted that the spins of Ni1 ions are nearly parallel to the $a^*$-axis ($\theta < 5^\circ$) at $T < T_N$ which is also the direction of applying fields in our experiments. Due to this complicated spin configuration, it is possible that different spin sublattices respond differently to the applied magnetic field.

On the basis of this concept, we propose a simplified spin-flip model to explain our observed step-like transition. At low
fields, there are four Ni1 spins in a unit cell: two upward and two downward spins. When $H > H_c$, one downward spin flips to upward and causes a moment change, $\Delta M$, by $2m_{Ni}$ per unit cell. Since the $Z$-factor is 4, the $\Delta M$ per formula is one half of $m_{Ni}$, which is consistent with our results. A possible spin configuration of the high-field state is shown in figure 4(b), where the flipped spin is denoted by a green arrow with a star. In addition, the spin-flip transition usually shows a plateau at a high-field state; however our data show a monotonically increasing feature. It is possibly caused by the field dependence of the spins of Ni2 and Ni3 ions, which are tilted toward the field direction and produce the non-plateau high-field state. Furthermore, in the figure 4(b), there is still a downward Ni1 ion spin in a unit cell, suggesting a second transition which, correlated with another spin-flip behavior, possibly exists at higher field over 55 T. This simplified spin-flip model can only explain the $\Delta M$ of the low-temperature $M(H)$ curves. At higher temperatures, a thermal fluctuation or a complex out-of-plane spin arrangement might occur and reduce the $\Delta M$ values.

In the recent report of Pregelj et al., the 11 T transition was assigned as a spin-flop-like transition from an in-plane antiferromagnetic phase to a complex out-of-plane spin arrangement. Our measurements were carried out only in the $a^*$-direction; therefore, we cannot observe the effect of the out-of-plane spin arrangement directly. They also predicted that the transition field will increase with increasing temperature. However, our results show that the temperature dependence of the transition field is negligibly weak, but the $\Delta M$ is strongly affected by a thermal fluctuation. Furthermore, they predict that a ferromagnetic ordering phase of [Ni$_2$O$_7$X$_2$] units will exist above 24 T. However, we do not observe the transition in the region $H_c < H < 55$ T, indicating that the model proposed by Pregelj et al requires further improvements.

4. Summary

High-field magnetization curves of Ni$_5$(TeO$_3$)$_4$X$_2$ (X = Br, Cl) were measured at different temperatures. The two samples showed similar field-dependent behaviors at various temperatures. A step-like transition was observed at 11 T (10 T) for X = Br (Cl), which was consistent with other studies using ESR spectroscopy or magnetization measurements. At around 24 T, we did not observe any sign of another transition, which was inconsistent with the prediction by Pregelj’s report [10]. From $M(H)$ curves, we found that $\Delta M$ per formula is close to one half of $m_{Ni}$. We proposed a simplified spin-flip model to explain the step-like transition, which also suggested that a further transition could exist in the range higher than 55 T. Further magnetization measurements at higher fields and a more general spin-flop model are necessary.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas ‘High Field Spin Science in 100 T’ (No. 451) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References

[1] Shores M P, Nytko E A, Bartlett B M and Nocera D G 2005 J. Am. Chem. Soc. 127 13462–3
[2] Morita K, Yano M, Ono T, Tanaka H, Fujii K, Uekusa H, Narumi Y and Kindo K 2008 J. Phys. Soc. Japan 77 043707
[3] Johnsson M, Tomroos K W, Lemmens P and Millet P 2003 Chem. Mater. 15 68–73
[4] Millet P, Bastide B, Pashchenko V, Gnatchenko S, Gapon V, Ksari Y and Stepanov A 2001 J. Mater. Chem. 11 1152–7
[5] Zorko A, Arcon D, Dolinsek J, Jaglicic Z, Jeromen A, van Tol H, Brunel L C and Berger H 2007 J. Phys.: Condens. Matter 19 145278
[6] Pregelj M, Zorko A, Berger H, van Tol H, Brunel L C, Ozarowski A, Nellutla S, Jaglicic Z, Zaharko O, Tregenna-Piggott P and Arcon D 2007 Phys. Rev. B 76 144408
[7] Arcon D, Zorko A, Pregelj M, Dolinsek J, Berger H, Ozarowski A, van Tool H and Brunel L C 2007 J. Magn. Magn. Mater. 316 e349–51
[8] Pregelj M, Arcon D, Zorko A, Zaharko O, Brunel L C, van Tool H, Ozarowski A, Nellutla S and Berger H 2008 Physica B 403 950–1
[9] Mihály L, Fehér T, Dóra B, Náfrádi B, Berger H and Forró L 2006 Phys. Rev. B 74 174403
[10] Pregelj M, Zorko A, Zaharko O, Bousier R, Berger H, Katori H A and Arcon D 2009 Phys. Rev. B 79 064407