High-field magnetization of a two-dimensional spin frustration system, $Ni_5(TeO_3)_4X_2$ (X = Br, Cl)

2009 J. Phys.: Condens. Matter 21 436005

(http://iopscience.iop.org/0953-8984/21/43/436005)

J. Phys.: Condens. Matter **21** (2009) 436005 (4pp) doi:10.1088/0953-8984/21/43/436005

High-field magnetization of a two-dimensional spin frustration system, $Ni_5(TeO_3)_4X_2$ (X = Br, Cl)

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

Abstract

The high-field magnetization, $M(H)$, of $Ni_5(TeO_3)_4X_2$ (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 $T_N \sim 28$ and 23 K for X = Br and Cl, respectively. When $T < T_N$, we observe step-like transitions, at $H_c \sim 11$ 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.

$Ni_5(TeO_3)_4X_2$ (X = Br, Cl) is a new series compound with the Kagome spin system, having a well separated 2D layer structure in which the $[Ni_5O_{17}X_2]$ 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 $Ni_5(TeO_3)_4Br_2$, showing $g_{\parallel} = 2.45$ and $g_{\perp} = 2.53$ [5]. Recently, noncollinear arrangements of the Ni sublattices of $Ni_5(TeO_3)_4Br_2$ 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 ∼10.7 and 10 T for X = Br and 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 $Ni_5(TeO_3)_4Br_2$ in magnetic fields up to 12 T. A transition peak was observed in the dM/dH curve at ∼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 = Br (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, as 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 ∼38 and 17 mg for X = Br and Cl, respectively. Magnetic field is applied perpendicular to the crystalline surface, i.e. the magnetic field is oriented along the a^*-axis, where a^* 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 $Ni_5(TeO_3)_4Br_2$ at 1.5 K. A step-like transition can be clearly seen at $H_c \sim 11$ T. When $H > H_c$, the $M(H)$ curve shows a monotonic linear increase, which shows neither saturation nor a plateau behavior up to $H \sim 55$ T. In figures 1(b) and (c), we show the $M(H)$ curves at different temperatures for X = Br and 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

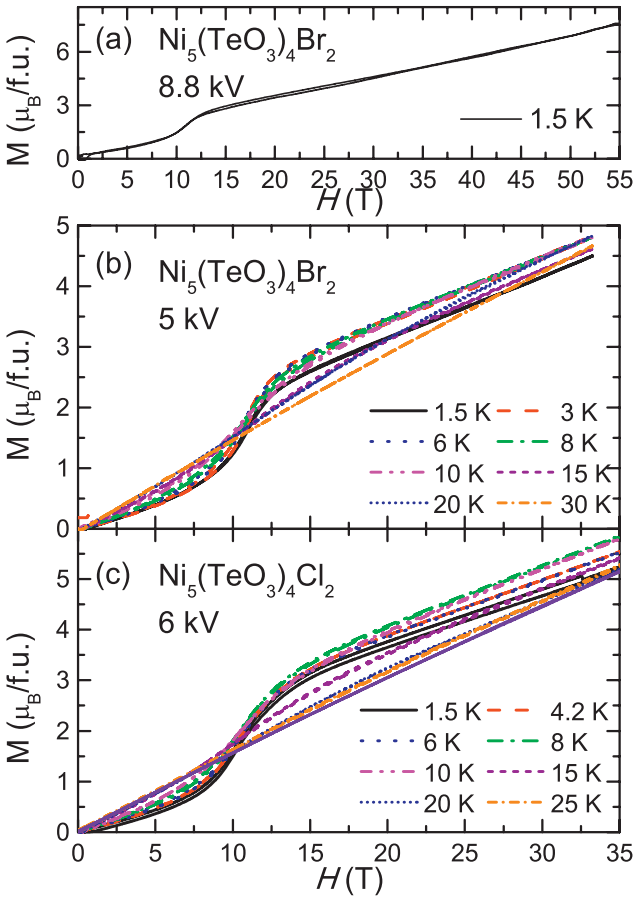

Figure 1. (a) $M(H)$ for $Ni_5(TeO_3)_4Br_2$ at 1.5 K. ((b), (c)) $M(H)$ curves for $Ni_5(TeO_3)_4Br_2$ and $Ni_5(TeO_3)_4Cl_2$ at some selected temperatures.

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 = Br sample. However, there remains a very weak and broad peak at $T > T_N$ (i.e. 25 K) for the X = Cl sample. It is possibly related to some short-range ordering component which presents at $T > T_N$. Second, in the case of X = 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 = 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 (ΔM) can be roughly determined from the $M(H)$ curves. In figure 3, we show a

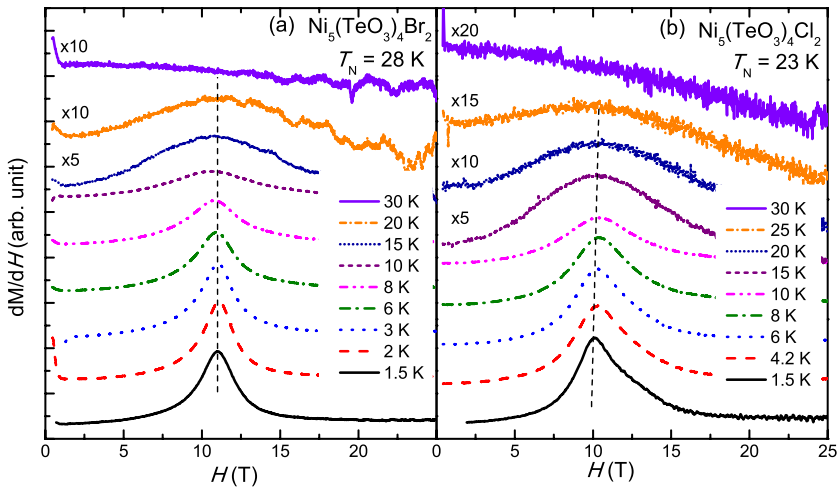

Figure 2. dM/dH curves for $Ni_5(TeO_3)_4Br_2$ and $Ni_5(TeO_3)_4Cl_2$ at some selected temperatures.

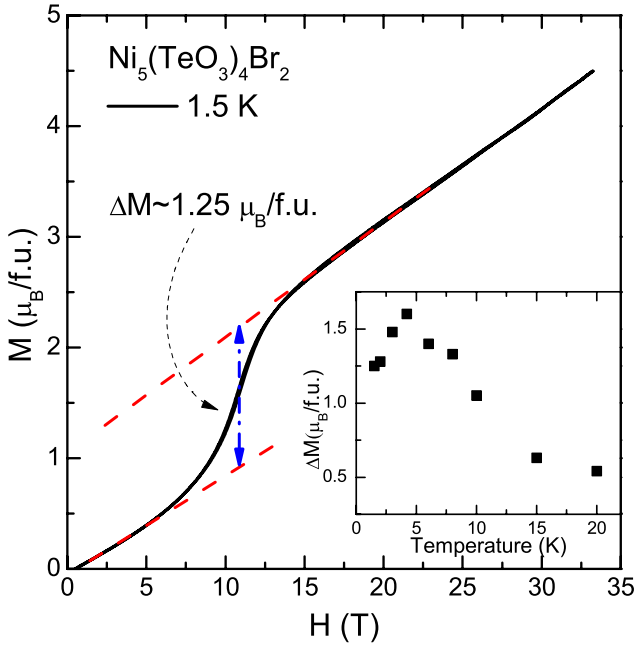

Figure 3. Typical plot for determining ΔM. The red dashed line is to guide the eye. The inset shows the temperature-dependent ΔM.

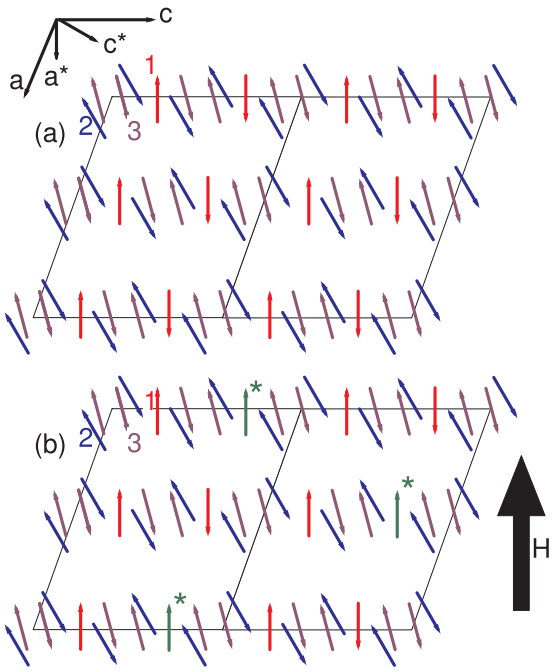

Figure 4. (a) Sketch of the spin configuration at low field of the samples studied (*ac* projection) [6]. Red, purple, and royal blue arrows represent the spin orientations of Ni1, Ni2, and Ni3 ions. (b) Sketch of the high-field spin configuration. The large arrow denotes the direction of the applied magnetic field.

typical example of an X = Br sample at 1.5 K, for which the ΔM is ∼1.25 μ_B/formula. The ΔM value increases with decreasing temperature and slightly decreases below 5 K (see the inset of figure 3). Interestingly, the ΔM 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 ($\theta < 5°$) 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, ΔM, by $2m_{Ni}$ per unit cell. Since the Z-factor is 4, the ΔM 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 ΔM 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 ΔM 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 ΔM is strongly affected by a thermal fluctuation. Furthermore, they predict that a ferromagnetic ordering phase of $[Ni_5O_{17}X_2]$ 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 $Ni_5(TeO_3)_4X_2$ (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 ΔM 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.

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