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Magnetism in the novel spin system $Ni_5(TeO_3)_4Br_2$ with two-dimensional frustrated geometry

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Abstract

A study of magnetism in the novel 2D spin system $Ni_5(TeO_3)_4Br_2$, featuring a frustrated triangular geometry, is presented. We combine magnetization, heat capacity and high-field electron spin resonance measurements to investigate a long-range magnetic ordering below $T_N = 29$ K. Additional peculiar behaviour, most likely related to the spin system, is observed below $T' = 14$ K.

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

1. Introduction

Geometrical frustration in a spin system, which precludes the possibility that all pair-wise antiferromagnetic (AF) interactions are satisfied simultaneously, has been recognized as the key promoter of novel ground states and exotic magnetic phenomena. Likewise, a reduced dimensionality and a quantum nature of spins ($S = 1/2, 1$) enhance AF fluctuations and thus, in principle, suppress long-range ordering (LRO). Extensive experimental and theoretical research in this field during the last couple of decades resulted in an enormous amount of novel concepts and newly developed experimental techniques, applicable to discovered or rediscovered materials. However, it is still a major challenge to understand the competition between these effects and the magnetic anisotropy encountered in real systems, which tends to drive the systems towards LRO.

These mechanisms are, for instance, effective in a two-dimensional (2D) kagome lattice, where in the case of $S = 1/2$ spins the ground state could well be the long-sought resonating-valence-bond (RVB) state [1, 2]. The experimental research in this field has been rather limited due to a lack of a suitable $S = 1/2$ system with a pure kagome geometry, which has been

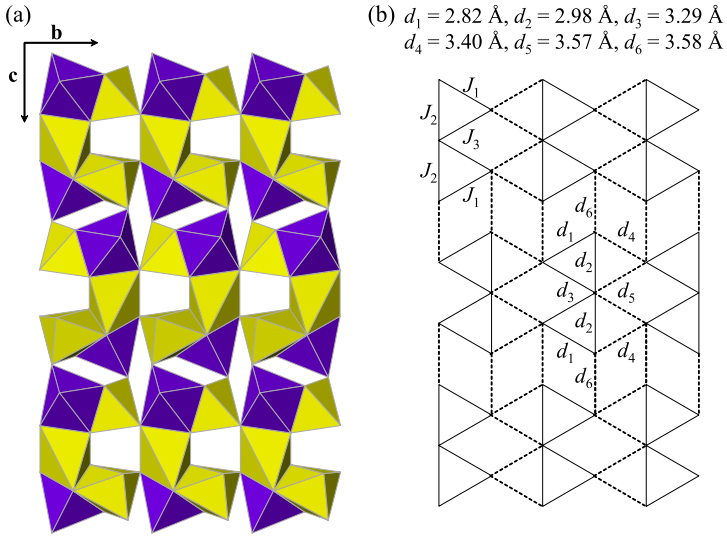

Figure 1. (a) Arrangement of NiO_6 (light-yellow) and NiO_5Br (dark-purple) octahedra within the *bc* crystal plane of $Ni_5(TeO_3)_4Br_2$. (b) The corresponding 2D spin lattice with the Ni–Ni distances and presumably dominant exchange $J_{1,2,3}$.

synthesized only recently [3]. Until now, the experimentalists have been focused on different 'approximants', such as the $S = 3/2$ kagome-bilayer compound $SrCr_9Ga_3O_{19}$ [4] and the $S = 1/2$ kagome-like compound $Cu_3V_2O_7(OH)_2{\cdot}2H_2O$ [5], both exhibiting strong fluctuations in their ground state [4, 6]. In addition, many other frustrated triangular geometries have been discovered. In fact, many of them, such as mineral spinels and pyrochlores [7, 8], are quite common in nature [8].

Recently, Johnsson *et al* have reported the successful isolation of new members of the ternary phase system NiO–$NiCl_2$–TeO_2 [9]. The $Ni_5(TeO_3)_4X_2$ (X = Cl, Br, I) compounds were synthesized by employing lone-pair cations Te(IV), which effectively led to a peculiar 2D spin structure, where buckled Ni^{2+} ($S = 1$) layers were connected only through TeO_3X tetrahedra. According to the crystal structure, $Ni_5O_{17}X_2$ claw-shaped entities as building blocks (figure 1(a)), featuring a frustrated triangular geometry, should determine units of strongly coupled Ni spins since the intra-claw Ni–Ni distances are short [9] and the connection between highly distorted NiO_6 and NiO_5X octahedra is provided by face- and edge-sharing, in contrast to corner-sharing between neighbouring claws within each layer. Due to different types of sharing and Ni–Ni distances, dissimilar exchange constants are expected within each claw (figure 1(b)).

In these systems a strong competition between LRO and frustration, enforced by magnetic anisotropy, is expected. We have initiated a comprehensive magnetic study on the $Ni_5(TeO_3)_4Br_2$ single-crystal samples in order to elucidate the ground state and low-lying magnetic excitations. In this paper, we report on our findings based on magnetization, specific heat and high-field electron spin resonance (ESR) measurements.

2. Experimental details

The experiments were carried out on $Ni_5(TeO_3)_4Br_2$ single-crystal samples with a plate-type geometry. The quality of the samples was checked and the orientation of the crystal axes

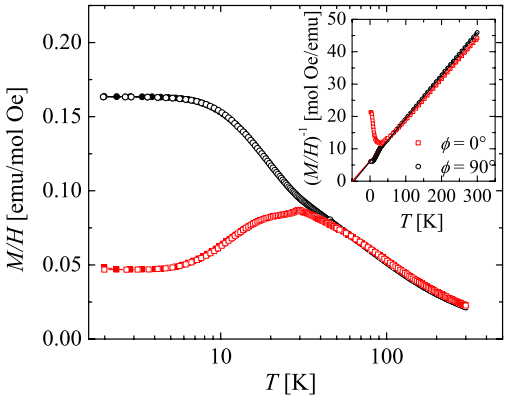

Figure 2. Magnetization of the $Ni_5(TeO_3)_4Br_2$ spin system for the magnetic field $H = 0.1$ T perpendicular ($\phi = 0°$) and within the Ni layers ($\phi = 90°$) in ZFC (open symbols) and FC (full symbols) runs. The inset shows the agreement of the inverse magnetization with the Curie–Weiss dependence (solid lines) for both orientations.

Table 1. Curie–Weiss parameters of the magnetization in $Ni_5(TeO_3)_4Br_2$ above 100 K.

ϕ (deg)	θ (K)	C (A m^2 K mol^{-1} T^{-1})	$\mu_{\rm eff}/\mu_{\rm B}$	g
0	−49.8	79.3	3.56	2.52
90	−49.5	75.2	3.46	2.45

was determined from x-ray diffractograms. Bulk DC magnetic measurements were performed with a Quantum Design SQUID magnetometer in a static magnetic field of 0.1 T in zero-field-cooled (ZFC) and field-cooled (FC) runs between room temperature and 2 K. Specific heat was measured on a home-built adiabatic calorimeter between 7 and 35 K. High-field ESR measurements were conducted on a home-built spectrometer at NHMFL, with a gunn-diode source working at the Larmor frequency of 240 GHz.

3. Results and discussion

3.1. DC magnetization

The bulk DC magnetization exhibits a Curie–Weiss dependence at temperatures above 100 K; $M/H = C/(T - \theta)$ with the Curie constant $C = 5N_{\rm A}\mu_{\rm eff}^2/3k_{\rm B}$ (inset to figure 2). The minor differences between the measurements recorded with the external magnetic field parallel to the normal of the bc crystal plane ($\phi = 0°$) and within the Ni layers ($\phi = 90°$) is attributed to g-factor anisotropy (table 1). The obtained values $g_\parallel = 2.28$ and $g_\perp = 2.45$ are close to the value reported for powder [9] and common for octahedrally coordinated Ni^{2+} ions. The Weiss temperature $\theta = -50$ K corresponds well to both orientations. Its sign is in line with the expected dominant AF Ni spin–spin interaction.

Below 50 K a pronounced angular dependence of the magnetization is observed. For the magnetic field perpendicular to the Ni layers a broad maximum appears around 30 K. In addition, a well-defined narrow peak is present at $T_{\rm N} = 29$ K, which can be attributed to the onset of LRO, as further discussed below. This transition is evidenced as an inflection point at the same temperature also for the magnetic field applied within the Ni layers. In contrast to the magnetization data of powder samples [9], almost no irreversibility between ZFC and FC runs

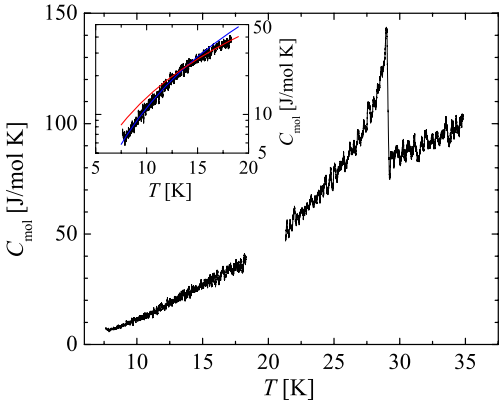

Figure 3. Heat capacity of $Ni_5(TeO_3)_4Br_2$ in zero magnetic field. The inset illustrates a modification of the power in the T^p dependence (smooth lines) around 14 K.

is present for single-crystal samples in both directions, excluding the possibility of some kind of frozen short-range-ordered state at low temperatures. Another interesting characteristic of the magnetization is the fact that it levels off at angle-dependent non-zero values below 5 K, which indicates a complex magnetic order possibly displaying weak ferromagnetic behaviour.

3.2. Heat capacity

Heat capacity measurements give support to the LRO setting in below $T_N = 29$ K (figure 3). It is hard to accurately determine the phonon contribution from these data. Therefore, the entropy increase associated with the peak at T_N can only be estimated to be of the same order as $\Delta S = 5N_A k_B(2S + 1) = 45.8$ J mol^{-1} K^{-1}, indicating that the majority of the Ni spins are cooperating in the magnetic ordering. In addition, another anomalous feature is observed at $T' = 14$ K, where the power of the T^p dependence changes from 2.3 to 1.7 when raising the temperature. As the phonon contribution becomes progressively important with increasing temperatures, an opposite behaviour is expected if due to phonons. This anomaly could thus originate from the magnetic system itself, where spin reorientation or additional freezing may occur around T'. It should be mentioned that the power $p = 2$ is typical for an ordered quasi-2D antiferromagnet; however, it is also found in kagome systems with no sign of magnetic ordering [8].

3.3. High-field ESR

Interestingly, the temperature $T' = 14$ K coincides well with the occurrence of high-field ESR spectra in $Ni_5(TeO_3)_4Br_2$. We have already reported that the ESR signal is observed only below 15 K due to extreme, i.e., seemingly diverging, broadening of the spectra when approaching that temperature [10]. In addition, the ESR spectra are characterized by a zero-field gap of 410 GHz and are thus significantly shifted from the line position expected in a paramagnet.

In figure 4 we show the angular dependence of the ESR spectra recorded at 240 GHz and at 5 K, i.e., well below the ordering temperature. The resonance-field position exhibits a minimum when the magnetic field is parallel to the normal of the Ni layers ($\phi = 0°$) and shifts towards higher fields on changing the angle. The signal disappears from the observation window (0–14 T) around $\phi = 50°$ and appears symmetrically around 130° (not shown in figure 4). Such angular dependence can be due to a crystal-field splitting of the energy levels

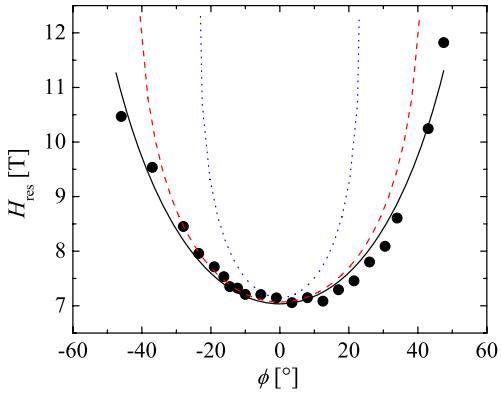

Figure 4. ESR resonance field in $Ni_5(TeO_3)_4Br_2$ recorded at 240 GHz and 5 K (●). Angle ϕ is measured with respect to the normal of Ni layers. Modelling includes the $1/\cos\phi$ dependence of the AFMR mode (——) as well as the crystal-field splitting effect of single-Ni-spin (· · · · · ·) and five-Ni-spin non-collective (- - - -) excitations.

within the system of five exchange coupled Ni spins, i.e., within the claw, if these are not taking part in the cooperative LRO. Alternatively, it can be due to an antiferromagnetic-resonance (AFMR) mode. In either case, the direction perpendicular to the Ni layers is assigned as the easy axis of the magnetic anisotropy while the hard axis lies within the Ni layers, which is also in line with the magnetization measurements. However, due to a pronounced temperature dependence of the resonance field at a fixed frequency [10], the AFMR is more plausible. The AFMR behaviour of the resonance field can be phenomenologically described with the $1/\cos\phi$ angular dependence, as already reported for other systems [11]. However, it should be stressed that the spin-lattice is non-bipartite in $Ni_5(TeO_3)_4Br_2$. Lastly, the observed angular dependence does not seem to be in agreement with a model of isolated fluctuating Ni spins (with crystal-field split levels) within the ordered states (figure 4).

It is expected that the LRO be significantly suppressed in the $Ni_5(TeO_3)_4Br_2$ spin system, due to both the frustrated geometry of the spin lattice and its reduced dimensionality. However, the results of the complementary experimental techniques presented in this paper speak strongly in favour of the LRO at rather high temperatures. The ordering temperature $T_N = 29$ K is not that far from the Weiss temperature $|\theta| = 50$ K, which is a rough measure of the general AF interaction strength. The geometric frustration must thus be hindered by a strong mechanism favouring the LRO. Such a mechanism can be provided by large magnetic anisotropy. Significant single-ion anisotropy is expected in $Ni_5(TeO_3)_4Br_2$ because of the strongly disordered nickel octahedra. In addition, the low symmetry of the spin lattice and significant g-factor shift from the free electron value $g_0 = 2.0023$ allow for the Dzyaloshinsky–Moriya interaction, which can be of the order of $\Delta g/g \cdot J$. In general, it causes nonlinear spin configurations, which could be responsible for the peculiar magnetization dependence below T_N.

4. Conclusions

We have presented a study of the novel 2D compound $Ni_5(TeO_3)_4Br_2$. Although the spin network should be highly frustrated by the geometry, the system shows clear evidence of collective magnetic ordering at $T_N = 29$ K. We speculate that this is due to strong magnetic anisotropy suppressing the spin fluctuations. The preferred orientation of the

spins is perpendicular to the Ni layers. However, as the local symmetry is rather low, a complicated spin arrangement is expected. Additionally, the magnetic system may undergo further rearrangements below $T' = 14$ K, as evidenced from both the heat capacity and the high-field ESR measurements, implying the competition between the spin fluctuations and the LRO, the former governed by the low-dimensional frustrated geometry and the latter endorsed by the magnetic anisotropy.

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