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Low-temperature magnetic and thermal properties of the frustrated two-dimensional $S = 1$ compound $Ni_5(TeO_3)_4Cl_2$

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The temperature and magnetic field dependent magnetization of the two-dimensional quantum spin system $Ni_5(TeO_3)_4Cl_2$ has been investigated using single crystals in temperature range 1.8–100 K and in magnetic fields up to 14 T. The magnetization below the magnetic phase transition demonstrates an unusual temperature behavior with considerable anisotropy. Combined magnetization and specific heat data allowed to determine the critical temperature of the magnetic phase transition, $T_c = 28.4$ K. Magnetic fields shift this temperature toward lower temperatures.

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75.60.Ej Magnetization curves, hysteresis, Barkhausen and related effects;
65.40.–b Thermal properties of crystalline solids.

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Low-dimensional magnets with frustrated interactions have been the subject of intensive research in last decades as they realize many types of phases, and an interplay of quantum and thermal fluctuations, as well as the effect of spin anisotropies. This also lead to search and synthesis of new compounds with specified features.

One of recently synthesized new compounds is the tellurium oxychloride $Ni_5(TeO_3)_4Cl_2$ [1]. It has a monoclinic symmetry with the space group $C2/c$ [1] with cell parameters at 153 K $a = 19.5674$ Å, $b = 5.2457$ Å, $c = 16.3084$ Å, $\beta = 125°29'$, $z = 4$. $Ni_5(TeO_3)_4Cl_2$ has a peculiar 2D spin structure with buckled Ni^{2+} layers. Nickel layers lie in the *bc* plane and form a rather complicated triangular structure with three different crystallographic Ni positions. Fragments of the crystalline structure are shown in Fig. 1. It is seen (Fig. 1,*b*) that distances and, evidently, exchange parameters may be different for different bonds. This might lead to a partial lifting of the degeneracies due to geometrical frustration. These circumstances may significantly effect on ground state of Ni^{2+} ion and magnetic properties of this compound.

The preliminary studies of the magnetic properties of $Ni_5(TeO_3)_4Cl_2$ performed on powdered [1] material demonstrate that at rather high temperatures the susceptibility can be described by the Curie–Weiss law with a negative constant $\Theta \approx -50$ K. This suggests that exchange interaction is of antiferromagnetic character. The temperature dependence of the susceptibility at $T \approx 23$ K exhibits an anomaly which the authors relate to a transition into an antiferromagnetic ordered state. The effective *g* factor determined from the dependence $\chi(T)$ was 2.21. In addition, at temperatures below 23 K the authors of [1] observed the pronounced dependence of magnetic susceptibility on experimental conditions (ZFC and FC dependences of $\chi(T)$).

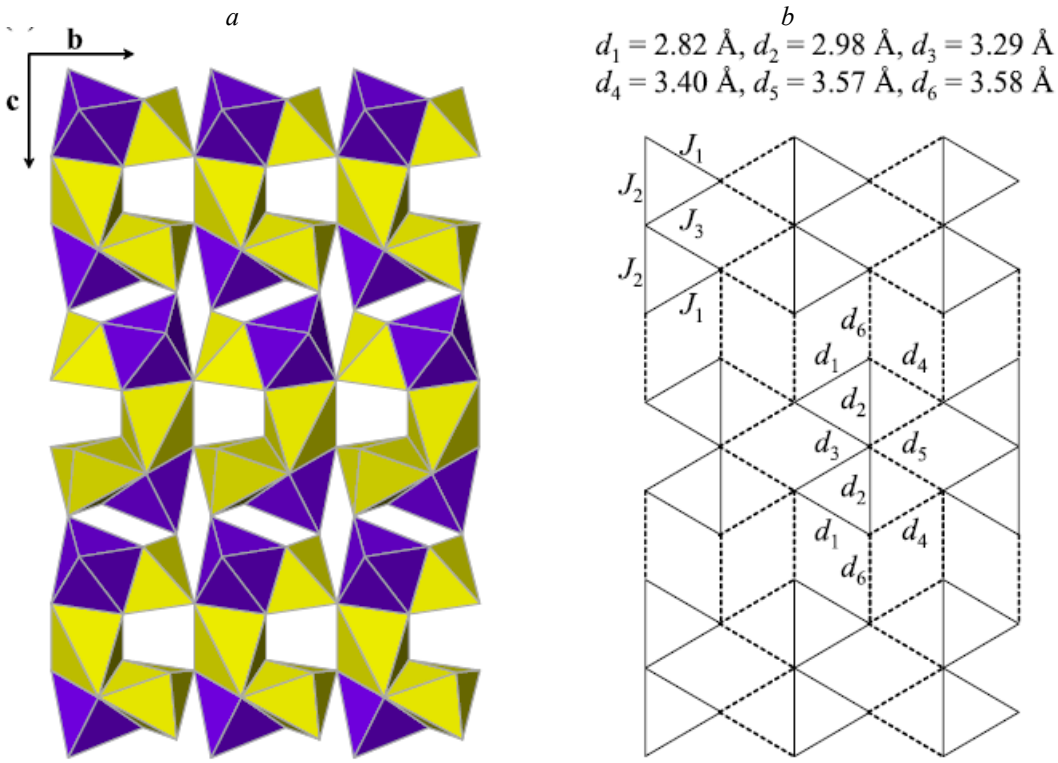

Fig. 1. a — Arrangement of NiO_6 (light) and NiO_5Br (dark) octahedra within the *bc* crystal plane of $Ni_5(TeO_3)_4Cl_2$. *b* — The corresponding 2D spin lattice with the Ni–Ni distances and presumably dominant exchange interactions J_1, J_2, J_3 (taken from [3]).

Recently [2] we investigated the magnetic and resonant properties of single crystalline $Ni_5(TeO_3)_4Cl_2$ samples along and perpendicularly to the easy magnetization axis a^* directed perpendicular to the *bc* crystallographic plane. Two pronounced anomalies on temperature dependence of magnetic susceptibility at $T_1 \approx 21$ K and $T_2 \approx 30$ K have been detected. In accordance with [1] we associate the anomaly at 21 K with a phase transition into an antiferromagnetic state. The origin for the anomalies at 30 K remains unclear. In addition, due to technical reasons the measurements were done in fact only along the easy magnetization axis a^*. The second direction perpendicular to it did not coincide with a magnetic axis in the *bc* plane. No difference in the results for different modes of cooling (FC, ZFC) was observed. To clarify the phase transition temperature and to complete the magnetization measurements, especially in high magnetic fields, further investigations were required.

This paper presents a careful investigation of the magnetic and thermal properties of oriented $Ni_5(TeO_3)_4Cl_2$ single crystals. The magnetizations measurements were performed in the temperature range 1.8–100 K using a vibrating sample magnetometer in a permanent magnetic field up to 14 T. The sample with the shape of a thin plate ($m = 14.1$ mg) was oriented by means of x-ray scattering on the STOE spectrometer. The specific heat investigation was made by use of PPMS devise in the temperature range 1.8–300 K in zero and 9 T magnetic fields. Magnetic field was applied along the a^* axis.

Results and discussion

Magnetic measurements

Measurements of the magnetic susceptibility were performed along the three principal magnetic axes. The axis of easy magnetization a^* is directed perpendicular to the crystallographic *bc* plane, which coincides with the plane of the sample. The *b* and *c* magnetic axes coincide with the corresponding crystallographic ones. Figure 2 present the temperature dependences of the susceptibility of a $Ni_5(TeO_3)_4Cl_2$ single crystal along the principal magnetic

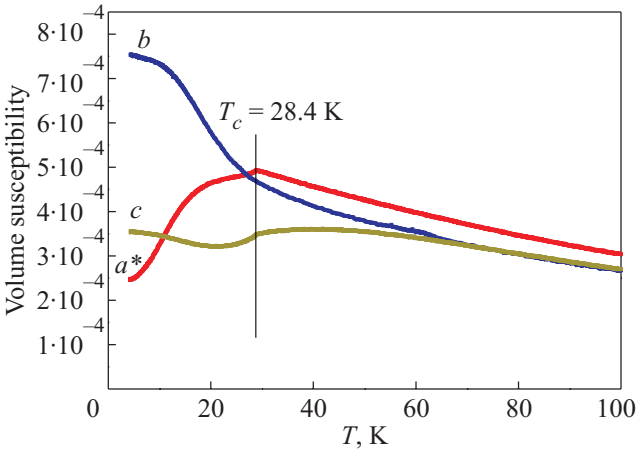

Fig. 2. Temperature dependence of magnetic susceptibility of single crystalline $Ni_5(TeO_3)_4Cl_2$ along the principal magnetic axes in a magnetic field 2 T.

axes in magnetic field 2 T. Distinct peculiarities of the susceptibility are observed at T_c = 28.4 K along a^* and c axes, but there is no evidence of any peculiarities along the b axis, the magnetization continues to grow. Comparing these results with results of the previous paper [2] we can say the following. The results of susceptibility measurements along the a^* axis are almost identical (as in [2] we see also an anomaly at 21 K), except that the maximum of temperature differ somewhat. This may be due to the poor accuracy of temperature measurement. The present result (T_c = 28.4 K) seems is more reliable, especially as it is confirmed by high-precision heat capacity data (see below). Measurements perpendicular to a^* axis in [2] were carried out along an accidental direction in the bc plane, so comparing them with those of that work seems incorrectly. Below 50 K the susceptibility becomes strongly anisotropic. Since the Curie–Weiss constant is negative [1,2], we deal with a dominant antiferromagnetic long-range ordering, however, the susceptibility behavior is very unusual for a collinear Neel-type antiferromagnet. In such a type of antiferromagnets the susceptibility orthogonal to the easy direction is almost constant for temperatures below T_N, while in our case the susceptibility along b axis continues to grow in the whole investigated temperature interval. This behavior cannot be explained by the presence of magnetic impurities in the sample, because our resonance data [2] doesn't indicate their presence. For the same reason the view point proposed in [4] for $Ni_5(SeO_3)_4Br_2$ which is very similar to $Ni_5(TeO_3)_4Cl_2$ is not applicable. These authors suggest that the sample consists of a mixture of two magnetic phases, the ordered and disordered. In our resonant measurements [2] we did not observe any additional phases except for the antiferromagnetically ordered one. But there are other possible reasons for the unusual behavior of the susceptibility in this compound. The first reason is strong and different single-ion anisotropy for the three crystallographically nonequivalent Ni^{2+} ions with distorted octahedra. The nonzero angular moment and low lattice symmetry permit the Dzyaloshinsky–Moriya interaction and as consequence week ferromagnetic moments in the bc plane. In general, it can lead to noncollinear magnetic structures may be with more than two sublattices. The next cause may be related to complicated exchange interaction responsible for antiferromagnetic ordering in this compound. The exchange interactions' paths in such an intricate structure are expected to be very sophisticated. As an example, the exchange-interaction model applied to $Ni_5(TeO_3)_4Cl_2$ introduces nine independent coupling constants [4]. And at last, frustration of magnetic bonds should also affect the magnetism of this compound, although the compound shows three-dimensional collective magnetic ordering. We believe that this is due to strong magnetic anisotropy that suppresses spin fluctuations.

The magnetization curves $M(H)$ of the single crystal $Ni_5(TeO_3)_4Cl_2$ was measured along the principal magnetic axes at T = 4.2 K in magnetic fields up to 14 T. The results are shown in Fig. 3. It is seen that even with the maximum available magnetic field of 14 T no saturation is observed along all magnetic axes. This may be connected with the strong exchange interaction (H_e = 21.3 T [2]). No observable hysteresis exists along the three axes. Along the a^* axis in magnetic fields of about 11 T there is an anomaly due to a spin reorientation transition. In AFMR experiments [2] on the frequency-field diagram a so-called "spin-flop" mode is observed with a transition field H_{sf} = 12 T. Although the fields are close, the width of $M(H)$ anomaly is very large, about 3.5 T. So it cannot be a simple spin-flop transition. Perhaps we are dealing with complex many sublattice magnetic structure, where the overturning of different sublattices takes place in different fields. Along the b axis the behavior is nonlinear but without remarkable anomalies. Magnetization along the c axis is practically linear up to the maximum available magnetic field. So the field dependencies of magnetization also demonstrate a complex magnetic order possibly with many noncollinear sublattices.

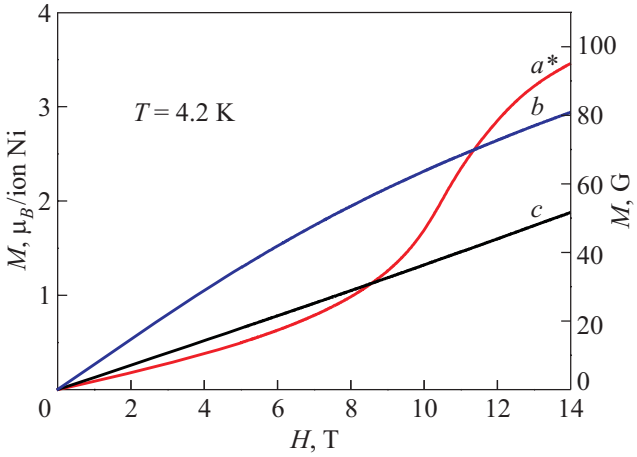

Fig. 3. Magnetization versus magnetic field of single crystalline $Ni_5(TeO_3)_4Cl_2$ along the principal magnetic axes.

Specific heat measurements

The specific heat investigation was made in the temperature range 1.8–300 K in zero and 9 T magnetic field. The results are given in Fig. 4. There is a sharp anomaly in the heat capacity at 28.42 K in zero applied magnetic field. This value perfectly coincides with the anomaly in the temperature dependence of the magnetic susceptibility. So we can conclude that the temperature T_c = 28.4 K is the critical temperature of the magnetic phase transition into three-dimensional ordered antiferromagnetic state. It must be noted that a magnetic field of 9 T applied along the a^* axis shifts the transition temperature to lower temperatures, T_c^* = 27.93 K (upper inset in Fig. 4). In the low-temperature regime, below 8 K, in the magnetic field 9 T

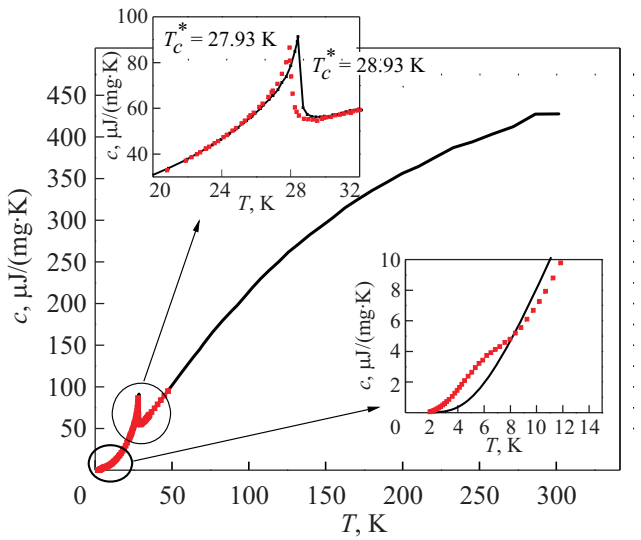

Fig. 4. Temperature dependence of the heat capacity of $Ni_5(TeO_3)_4Cl_2$: $H = 0$ (solid line), $H = 9$ T (symbols). The upper inset: region of specific heat anomaly, the right inset: low-temperature part.

some anomaly of the specific heat is observed (right inset in Fig. 4). The origin of this anomaly is yet unclear.

The phonon contribution to heat capacity is usually described within the Debye model. This model gives an adequate description of phonon specific heat at low temperatures, considerably lower than the Debye temperature θ_D, i.e., for the majority of materials for $T < 10$ K. We try to describe the low-temperature specific heat behavior and determine the Debye temperature. The θ_D temperature derived in the framework of the Debye model was determined by fitting the low-temperature dependence of specific heat to the experimental data. The specific heat is described by equation [6]

$$C_V = \frac{12}{5}\pi^4 n N_A k_B \left(\frac{T}{\theta_D}\right)^3 ,$$

where C_V is the lattice contribution to the molar specific heat, k_B is the Boltzman's constant, n is the number of atoms in the chemical formula of the studied compound, and N_A denotes the Avogadro number. The best fit is given using the Debye temperature $\theta_D = 158.7$ K.

Summary

1. The temperature dependencies of susceptibility of two-dimensional single crystalline $Ni_5(TeO_3)_4Cl_2$ was investigated along the principal magnetic axes.

2. The magnetization curves $M(H)$ along the principal magnetic axes was investigated in magnetic fields up to 14 T. The data indicates a complex nature of the magnetic reorientation transition.

3. The temperatures of the magnetic phase transition $T_c = 28.42$ K was identified, which was previously determined incorrectly. It was shown that magnetic fields shifts the transition temperature to lower temperatures.

4. An essential anisotropy of the magnetic susceptibility for temperatures below transition temperature was detected.

Acknowledgment

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