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Field-Induced Magnetic Order in Frustrated $TbBaCo_4O_7$ Single Crystals

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We present results of dc magnetic susceptibility measurements in $TbBaCo_4O_7$ single crystals performed at temperatures in the range 2–300 K and in magnetic fields up to 55 kOe. The results obtained seem to suggest that the ground state of $TbBaCo_4O_7$ is composed of coexisting long-range ordered and short-range ordered clusters and is transformed into a magnetically ordered weak ferromagnetic phase by application high magnetic field along c-axis.

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1. Introduction

Frustrated magnetic materials have recently attracted much interest, both theoretically and experimentally. This interest is related to the fact that the frustration is responsible for complete suppression of conventional magnetic order and appearance of various complex ground states, e.g. spin liquid [1] or spin ice states [2, 3]. The recently discovered [4, 5] family of mixed-valent compounds $RBaCo_4O_7$ (R — rare earth or Y) realizes a new class of two-dimensional geometrically frustrated magnets. Magnetic properties of these compounds are determined by their unique structure, which consists of 1:1 ordered stacking of triangular and kagome layers of CoO_4 tetrahedra. Cobalt ions are present in two charge states, Co^{3+} and Co^{2+}, respectively, in the ratio of 1:3 for stoichiometric compound. The ratio of the crystallographic sites in the triangular Co(1) and kagome Co(2) lattices is exactly the same.

In this paper we present results of dc magnetic susceptibility measurements in $TbBaCo_4O_7$ single crystals performed at temperatures in the range 2–300 K and in magnetic fields of up to 55 kOe. Only several studies of this material have been conducted until now (see e.g. [6, 7] for references), and still the exact nature of the magnetic ground state in the $TbBaCo_4O_7$ single crystals remains unclear. In Ref. [6] the presence of antiferromagnetic ordering in fields $H < H_c$ (where magnitude of H_c depends on temperature and magnetic field orientation) and a magnetic-field-induced ($H > H_c$) weak ferromagnetic component in the low-temperature range is suggested. In Ref. [7] no long-range magnetic ordering is reported. The results obtained in this paper seem to show that the ground state of $TbBaCo_4O_7$ is nonmagnetic, highly inhomogeneous, which is transformed into a weak ferromagnetic phase by application high magnetic field along c-axis. The main purpose of this paper is to clarify this problem.

2. Experimental

Single crystals of $TbBaCo_4O_7$ were grown by spontaneous crystallization method described in detail in [8]. The successful synthesis of single crystals made it possible to explain anisotropic properties of these materials. The crystal structure was investigated at room temperature by the powder X-ray diffraction method using a Siemens D5000 diffractometer with filtered Cu K_α radiation and a high resolution semiconductor detector Si[Li]. It was found that samples investigated are hexagonal (space group $P6_3mc$) with lattice parameters: $a = 6.3073$ Å, and $c = 10.2559$ Å. Magnetic measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS-5, Quantum Design).

The temperature dependences of inverse magnetic susceptibility $\chi^{-1}(T)$ in $TbBaCo_4O_7$ measured in magnetic field $H = 100$ Oe applied along the c-axis and in (ab) plane are shown in Fig. 1. It is seen that the temperature

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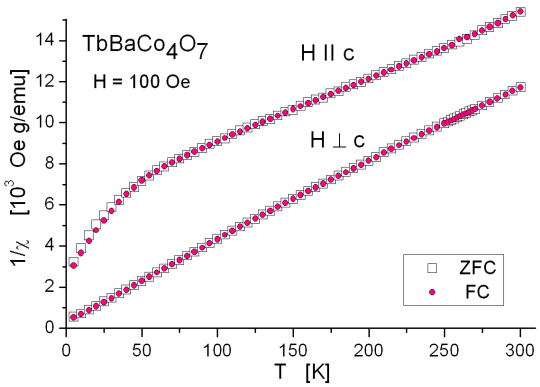

Fig. 1. Thermal variation of the inverse susceptibility in $TbBaCo_4O_7$, measured with a field $H = 100$ Oe directed parallel and perpendicular to the c-axis.

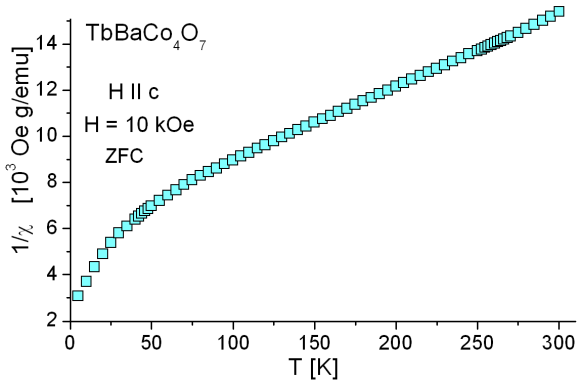

Fig. 2. Thermal variation of the inverse susceptibility in $TbBaCo_4O_7$, measured with a field $H = 10$ kOe directed parallel to the c-axis.

dependence $\chi(T)$ in wide temperature range can be well described by the Curie–Weiss law $\chi_i(T) = C_i/(T + \theta_i)$ with the paramagnetic Curie–Weiss temperatures equal to: $\theta_c = 158$ K for $H \| c$ and $\theta_{(ab)} = 12.5$ K for $H \perp c$. It has to be mentioned that very small temperature hysteresis of magnetization (the difference between field cooled (FC) and zero-field cooled (ZFC) susceptibilities) is observed. The positive Curie–Weiss temperatures indicate on antiferromagnetic interactions in the $TbBaCo_4O_7$ crystals. The difference between θ_c and $\theta_{(ab)}$ arises due to the crystal-field effects in frames of the single ion anisotropy model. This difference demonstrates that the system under consideration is highly anisotropic. It does not possess an easy axis anisotropy but rather has the easy plane anisotropy (perpendicular to the c-axis). The observed deviation of the inverse susceptibility $\chi^{-1}(T)$ from linearity below about 50 K (Fig. 2) for $H \| c$ is due to Tb^{3+} contribution. No such contribution is observed for $H \perp c$. It suggests Ising-like character of Tb^{3+} spins predominantly confined to point along the c-axis. Probably the ground state of Tb^{3+} is doublet with extremely anisotropic g-tensor in full analogy to the behavior of Tb_2TiO_7 crystals (see e.g. [9]). The Ising-like character of Tb^{3+} ions holds only at low temperature, because at higher temperatures a crossover to a Heisenberg-like behavior is expected since many crystal field levels become populated.

From the slope of $\chi^{-1}(T)$ one can determine magnetic moments p_{eff} of cobalt ions which have values: $p_{\text{eff}} = 1.5\ \mu_B$/Co for $H \| c$ and $p_{\text{eff}} = 1.58\ \mu_B$/Co for $H \perp c$. These results are consistent with low spin $S = 0$ states for Co^{3+} and low spin $S = 1/2$ states for Co^{2+} ions leading to $p_{\text{eff}} = 1.5\ \mu_B$/Co which almost agrees with the observations. Moreover, no change of spin state of cobalt ions is observed up to 300 K.

The influence of a magnetic field strength on a magnetization of the system was studied for two magnetic field orientations: $H \| c$ (Figs. 3 and 4) and $H \perp c$ (Fig. 5). Magnetization curves for $H \| c$ show very unusual field--induced jumps which are not observed in other members of the $RBaCo_4O_7$ family. In the low-field regime the magnetization varies linearly with field, but above a critical field the magnetization abruptly increases, and a field-induced state appears. The field-decreasing branch (curve 3) has small remanence (about $2 \times 10^{-3}\ \mu_B$/f.u.). Increasing the field once again produces a curve very near to the reverse leg of the first loop, demonstrating some hysteresis and the irreversibility of the transformation at the low temperature region. It means that the system was transferred to the ferromagnetic-like state.

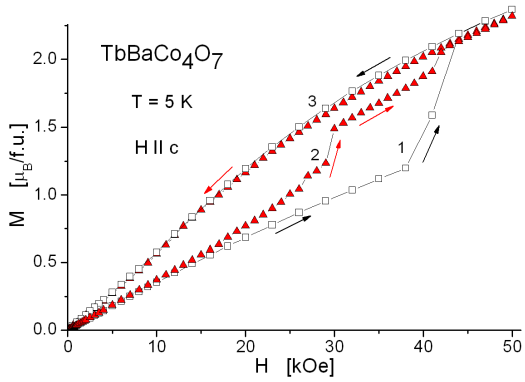

Fig. 3. Field dependence of the magnetization measured parallel to the c-axis at $T = 5$ K (details of experimental procedure given in the text).

To obtain once again magnetization jumps the sample should be warmed up to room temperature. It was shown that the magnitude of magnetic field and even number of the jumps depend critically on the magnetic field sweep rate used to record the data. For example, curve 2 was recorded using the magnetic field sweep lower than for curve 1. As the temperature is increased, the observed magnetization jumps decrease in magnitude (Fig. 4) and vanishes above 10 K. No magnetization jumps was observed for $H \perp c$. The nonlinear $M(H)$ dependence observed for $T = 5$ K (Fig. 5) is due to the spin–spin correlation function, displaying a short-range 120° configu-

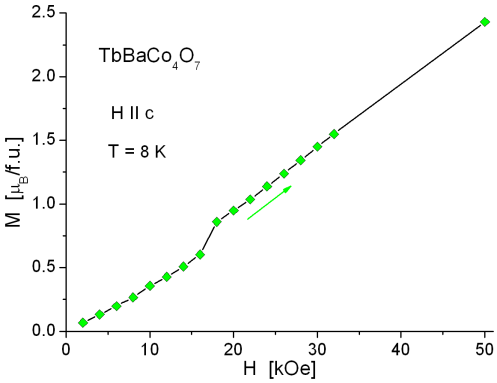

Fig. 4. Field dependence of the magnetization measured parallel to the c-axis at $T = 8$ K.

ration, decays rapidly as typically found in spin-liquids and observed also in $YBaCo_4O_7$ [10].

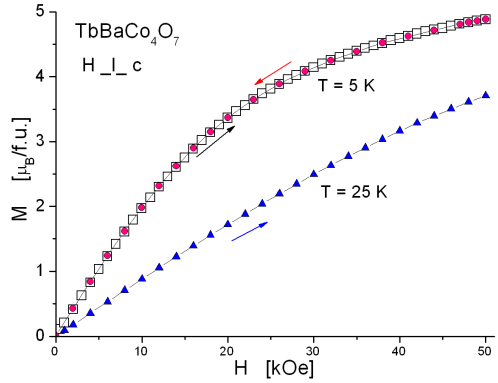

Fig. 5. Field dependence of the magnetization measured perpendicular to the c-axis at $T = 5$ K and $T = 25$ K.

3. Discussion and conclusion

The results obtained strongly suggest that $TbBaCo_4O_7$ compound possesses no long-range magnetic order down to helium temperature in a zero magnetic field. It was shown that in the currently measured temperature range the magnetic ordering (a weak ferromagnetic state) can be induced only by an applied magnetic field of around 3 T along c-axis. Such behavior seems to be due to strong geometrical frustration of the magnetic interactions and its failure to develop long-range order despite an antiferromagnetic Curie–Weiss temperature. We suggest that $TbBaCo_4O_7$ does not order in a zero magnetic field in contrast to other members of $RBaCo_4O_7$ family because of peculiar crystal field effect acting on Tb^{3+} ions. Similar situation was observed in kagome compound $Nd_3Ga_5SiO_{14}$ [11] and in the Heisenberg garnet $Gd_3Ga_5O_{14}$ which at low temperatures has a mixed ground state in zero field (see [12] and references therein). Similar behavior also was reported for the Ising garnet $Ho_3Ga_5O_{12}$ [13].

All the mentioned crystals have a mixed ground state that is composed of coexisting long-range ordered and short-range ordered clusters. The short range spin–spin correlations become of longer range as a field is applied. In frames of such *scenario* magnetization jumps observed in $TbBaCo_4O_7$ may be described as a transition from small to large clusters. Similar magnetic field-induced transitions in paramagnetic state were observed for the first time in $Sm_{0.65}Sr_{0.35}MnO_3$ manganites [14]. These observations confirm that proposed mechanism of magnetization jumps is realistic and corroborate unconventional character of the ground state. Definitive interpretation of the ground state character of the studied crystals from magnetization data alone is difficult because of the presence two magnetic subsystems. The results presented could also be considered in the frames of spin-liquid ground state. But we have not enough experimental data to support this hypothesis. Therefore a detailed neutron diffraction study on the $TbBaCo_4O_7$ crystals giving chance to solve finally this problem is presently underway.

Acknowledgments

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