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Abstract
Investigation of the crystal structure, magnetic ordering and magnetic properties of the compound $TbCo_{0.5}Mn_{0.5}O_{3.06}$ has been carried out by neutron powder diffraction and magnetization measurements. The Co and Mn ions are shown to have a partial NaCl-type crystallographic ordering in the B-sublattice of the ABO_3 perovskite. On the basis of the magnetization study, metamagnetic behaviour has been revealed. The critical fields of the metamagnetic transition have been found to decrease with the approach to the Curie point at 98 K. The neutron diffraction experiments suggest that the compound $TbCo_{0.5}Mn_{0.5}O_{3.06}$ consists of ferromagnetic and spin-glass-like phases. In the absence of an external magnetic field, a small ferromagnetic component appears in the Tb sublattice. The magnetic moments are directed antiparallel to the ferromagnetic component of the Co/Mn sublattice due to a negative f–d exchange polarization. Below 10 K a short-range antiferromagnetic order starts to develop in the Tb sublattice. The spin-glass-like phase associated with the random Co/Mn distribution transforms into the ferromagnetic phase under an external magnetic field, while in the Tb sublattice long-range magnetic order, being a superposition of the F, A, C, and G components, develops.

1. Introduction

The discovery of colossal magnetoresistance in the rare-earth hole-doped manganites has stimulated study in related compounds. The solids $LnCo_{0.5}Mn_{0.5}O_3$ (Ln—lanthanide) with a perovskite structure are attractive objects for investigation of the coupling between the degree of cationic ordering and the ground magnetic state. A rock salt-type ordering of the cobalt and

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manganese in the B-sublattice of the perovskite ABO_3 causes the appearance of ferromagnetism associated with the positive superexchange interaction of Co^{2+}–O–Mn^{4+} [1–3]. Partial destruction of the B-site crystallographic ordering achieved by means of both slight deviation from the equiatomic Co/Mn ratio or oxygen stoichiometry and specific heat treatment leads to a significant decrease of the magnetization and the Curie temperature [4–6]. The latter is explained by appearance of antiferromagnetic interactions of Co^{2+}–O–Co^{2+} and Mn^{4+}–O–Mn^{4+} in the B-site disordered clusters [2].

A peculiar feature of the partly ordered cobalt–manganese compounds is the existence of metamagnetic phase transitions. Metamagnetic phenomena in the $LnCo_{1-x}Mn_xO_{3+\delta}$ (Ln = Eu, Nd, and Y) series were investigated in [6], and H–T magnetic phase diagrams were proposed. On the basis of the magnetization measurements it was suggested that metamagnetism in the partly ordered cobalt–manganese perovskites was due to a field-induced transition from the ferrimagnetic phase, where the magnetic moments of Co^{2+} and Mn^{4+} ions were antiparallel, to the ferromagnetic one [6]. To verify this hypothesis we have performed a neutron diffraction study of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ perovskite under an applied magnetic field. It has been shown that application of an external magnetic field results in formation of the ferromagnetic state from the spin-glass-like component.

2. Experimental details

The $TbCo_{0.5}Mn_{0.5}O_{3+\delta}$ sample was prepared from the oxides Tb_4O_7, Co_3O_4 and Mn_2O_3 using standard ceramic technology. Reagents were mixed in a desired proportion and heated in air at $1000\,°C$ for 3 h and at $1320\,°C$ for 10 h with intermediate grinding. After a final heat treatment the sample was slowly cooled to room temperature at a rate of $50\,°C\,h^{-1}$ to ensure more complete absorption of oxygen by the lattice. Phase purity of the sample has been confirmed by x-ray diffraction data obtained with a DRON-3M diffractometer (Cu $K\alpha$ radiation).

The magnetization measurements were performed with a superconducting quantum interference device (SQUID; MPMS 5, Quantum Design). The neutron diffraction experiments were carried out at the Berlin Neutron Scattering Center (BENSC) using the fine resolution powder diffractometer E9 (FIREPOD) with a neutron wavelength of $\lambda = 1.7971$ Å. The diffractograms were obtained at temperatures of 300 and 1.6 K (without an applied magnetic field and in a field of 5 T). The data were analysed by the Rietveld method using the FullProf program [7]. The neuron diffraction estimation of the oxygen content led to a nominal chemical formula $TbCo_{0.5}Mn_{0.5}O_{3.06}$ with an error of ±0.01 oxygen per formula.

3. Results and discussion

3.1. Crystal structure

In accordance with the structural data obtained for the compounds $TbCoO_3$ and $TbMnO_3$ [8–10], Rietveld refinement of the neutron powder diffraction pattern of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ sample at $T = 300$ K was initially performed using the orthorhombic space group $Pbnm$, where Co and Mn randomly occupy only one crystallographic position 4b (0.5, 0, 0) for the B-sublattice element (figure 1(a)) [11]. However, this structural model has not allowed us to reproduce the increased intensity of the (101) reflection. Taking into account that the neutron scattering lengths of Co and Mn have opposite sign [12], this reflection must increase its intensity when the transition metals have an ordered arrangement in the perovskite lattice as shown in figure 1(b).

To test the possibility of ordering of the B-site cations, crystal structure refinement of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ compound was performed in the monoclinic $P2_1/n$ space group. This
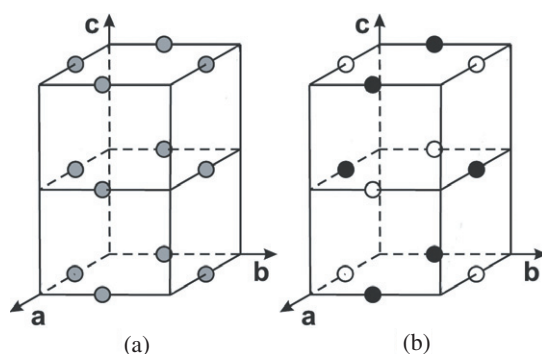
Figure 1. Schematic representation of the B-site elements in the unit cell of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ perovskite. (a) Space group $Pbnm$: Co and Mn randomly occupy crystallographic position 4b (grey circles). (b) Space group $P2_1/n$: Co and Mn are placed at positions 2c (black circles) and 2d (white circles), respectively.
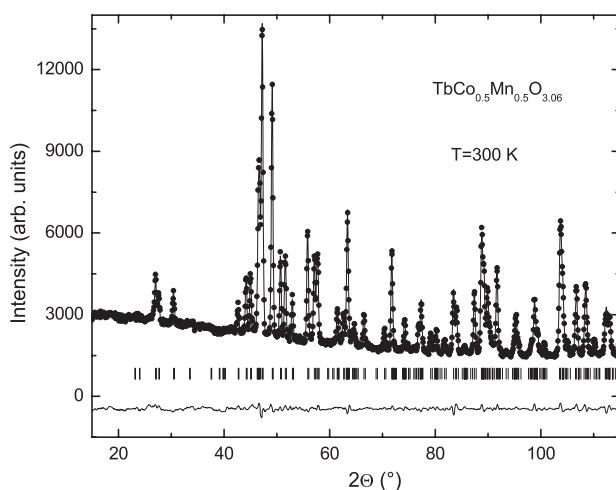

Figure 2. Rietveld refinement of the neutron powder diffraction pattern for the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ sample at $T = 300$ K. The difference between observed (solid circles) and calculated (solid line) spectra is plotted at the bottom. Bragg reflections are indicated by ticks.

group is a subgroup of the $Pbnm$ space group and has two non-equivalent positions for the transition metals: 2c (0, 0.5, 0) and 2d (0.5, 0, 0) [11]. Co and Mn atoms were placed at positions 2c and 2d, respectively, but the corresponding fit shows an excess increase in the theoretical intensity of the (011) and (101) peaks. After that, the possibility of the existence of antisite defects in the B-sublattice was considered [6, 13], and the best fit was achieved. The refinement has shown the presence of 35(3)% of the defects, i.e. 65% of Co and 35% of Mn are located at position 2c and 65% of Mn and 35% of Co are at position 2d. Good agreement between the observed and calculated diffraction patterns is shown in figure 2. The structural parameters, selected interatomic distances and angles are presented in table 1. The average B1–O and B2–O distances are 2.04 and 1.95 Å, respectively. Taking into account the model of the B-site cation distribution and the ionic radii of Co^{2+}, Co^{3+}, Mn^{3+}, Mn^{4+} and O^{2-} [14], one can suppose that the most appropriate ionic approximation for the compound under study
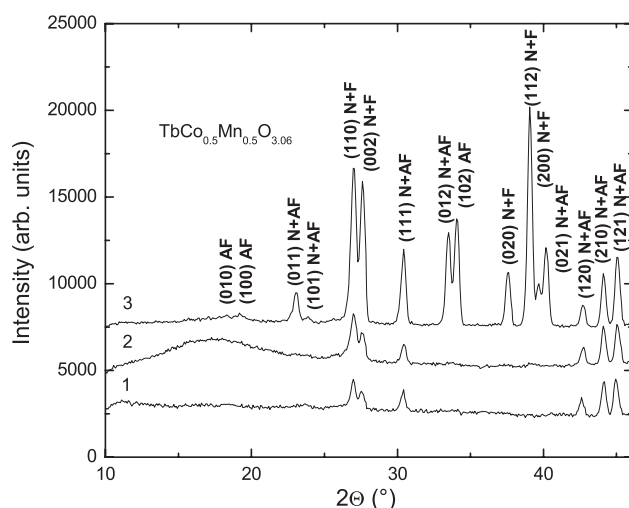
Figure 3. Experimental neutron powder diffraction patterns of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ sample at different temperatures: (1) $T = 300$ K; (2) $T = 1.6$ K; (3) $T = 1.6$ K, $B = 5$ T. N, F and AF—nuclear, ferromagnetic and antiferromagnetic contributions, respectively.

Table 1. The structural parameters, reliability factors and selected interatomic distances for the compound $TbCo_{0.5}Mn_{0.5}O_{3.06}$ at $T = 300$ K. B is the mixture of the transition metals Co and Mn with ratios of 0.65/0.35 and 0.35/0.65 for B1 and B2, respectively.

Cell (Å)	Atom	x	y	z	R-factors (%)	Distances (Å)	
	Tb 4e	0.5167(4)	0.5698(4)	0.2467(9)		B1–O1	2.002
$a = 5.2803(1)$	B1 2c	0	0.5	0	$R_p = 2.54$	B1–O2	2.055
$b = 5.5845(1)$	B2 2d	0.5	0	0	$R_{wp} = 3.27$	B1–O3	2.058
$c = 7.5163(1)$	O1 4e	0.3951(5)	0.9631(4)	0.2455(9)	$R_B = 4.35$	B2–O1	1.938
$\beta = 89.996(6)°$	O2 4e	0.1974(9)	0.1896(9)	−0.0481(9)	$\chi^2 = 2.70$	B2–O2	1.951
	O3 4e	0.3166(9)	0.7031(9)	−0.0523(9)		B2–O3	1.960

is $TbCo_{0.38}^{2+}Co_{0.12}^{3+}Mn_{0.5}^{4+}O_{3.06}$ rather than $TbCo_{0.5}^{3+}Mn_{0.38}^{3+}Mn_{0.12}^{4+}O_{3.06}$. These results agree with the data obtained for other $LnCo_{0.5}Mn_{0.5}O_{3+\delta}$ perovskites [15, 16].

3.2. Magnetic structure

The neutron diffraction pattern obtained at $T = 1.6$ K (in a magnetically ordered phase) has been used to refine the magnetic structure of the $TbCo_{0.5}Mn_{0.5}O_{3.06}$ sample. The additional intensity observed for the nuclear reflections with $h+k =$ even, $l =$ even indicates the presence of ferromagnetic ordering. No additional magnetic peaks and intensities corresponding to any type of antiferromagnetic order have been detected (figure 3). Initially we performed the calculations based on a model suggesting that the ferromagnetism vector is parallel to one of the crystallographic axes, but the model does not allow us to obtain an appropriate agreement between the experimental and theoretical diffraction profiles. It has been found that a ferromagnetic structure model with the non-zero components along all three axes gave a significantly better fit to the observed magnetic intensities.

The total magnetic contribution consists of a sum of magnetic contributions of both Co–Mn and Tb sublattices and the vector of magnetic moment of Tb sublattice ($\sim 0.63 \ \mu_B$) has

an antiparallel component towards the Co/Mn moment ($\sim$1.31 μ_B). The refinement gives components $M_x = 0.65(9)$, $M_y = 0.77(9)$, $M_z = 0.84(8)$ μ_B and $M_x = -0.28(8)$, $M_y = -0.51(8)$, $M_z = -0.23(7)$ μ_B for Co/Mn and Tb sublattices, respectively. The refined magnetic moments of the B-site ions are lower than those expected for the full spin arrangement, ($\sim$3 μ_B), suggesting a presence of the phase which does not give a coherent contribution to the magnetic neutron scattering (spin-glass or paramagnetic phase). One should note that characteristic features of a spin-glass state (the shift of a peak at the Curie point in the real part of the ac susceptibility with frequency and spin relaxation for $T < T_C$ as indicated by the time dependence of the remanent magnetization) have been reported for the compound La$_2$CoMnO$_6$ [17]. A typical spin-glass behaviour has been observed in the Gd$_2$CoMnO$_6$ perovskite [18].

A remarkable feature of the neutron diffraction pattern obtained for the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ compound at $T = 1.6$ K is the existence of a broad peak below $2\Theta \sim 22°$ (figure 3). Similar broad peaks have been observed in a neutron diffraction study of the compound TbMnO$_3$ [10]. It was concluded that the peaks are coming from short-range ordering of the Tb moments [10]. One may suppose that the short-range ordering of the terbium magnetic moments corresponds to the spin-glass-like phase of the Co/Mn sublattice rather than the paramagnetic phase, since the presence of the molecular field from the neighbouring Co/Mn ions is necessary to induce magnetic ordering in the Tb sublattice [5].

The diffraction profile at $T = 1.6$ K changes appreciably when the measurement is performed in the presence of an external magnetic field (figure 3). The plateau at small angles disappears, diffraction peaks increase their intensities and a number of reflections forbidden by the space group $P2_1/n$ arise. The observed additional intensity of the diffraction peaks shows the presence of F-type ($h + k =$ even, $l =$ even), A-type ($h + k =$ even, $l =$ odd), C-type ($h + k =$ odd, $l =$ even) and G-type ($h + k =$ odd, $l =$ odd) magnetic components which reflect the transition of the Co/Mn sublattice in the ferromagnetic state and the formation of long-range canting ordering of the Tb magnetic moments.

3.3. Magnetic properties

The temperature dependence of the magnetization of the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ compound is shown in figure 4. One can see that spontaneous magnetization begins to develop at $T_C = 98$ K. The zero field cooled (ZFC) curve passes through a maximum slightly below the Curie point and sharply deviates from field cooled (FC) magnetization with decreasing temperature. Such a behaviour of the ZFC dependence is characteristic of the cobaltites and lightly doped manganites and is attributed to the large magnetic anisotropy of these compounds [19]. The FC magnetization increases down to 40 K, then starts to decrease, and below 10 K increases again. Taking into account the results of the neutron diffraction experiments we may suggest that the decrease of the FC magnetization reflects the antiparallel ordering of the Tb magnetic moments towards Co/Mn ones due to f–d polarization (the contribution of the magnetic moments of rare-earth ions becomes apparent only in a low temperature region, typically below 30 K [5]), while the increase of the magnetization observed below 10 K corresponds to the development of short-range antiferromagnetic ordering in the Tb sublattice [10].

Increasing the field induces the appearance of a peak in the FC magnetization near the transition into the paramagnetic state (figure 5). The peak becomes less pronounced and shifts to lower temperatures as the field increases. An applied magnetic field induces metamagnetic transitions, as clearly observed in the $M(H)$ dependences (figure 6). The critical fields of the transitions are reduced with increasing temperature. Similar features have been observed in some previously studied LnCo$_{1-x}$Mn$_x$O$_{3+\delta}$ compounds [4, 6].
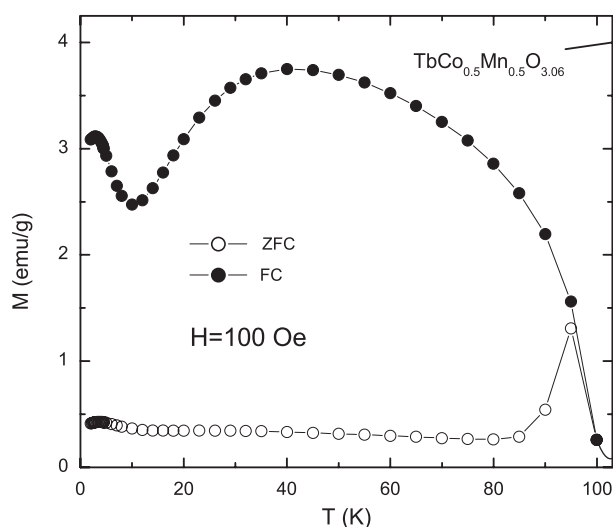
Figure 4. The temperature dependences of magnetization for the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ sample, measured at $H = 100$ Oe. Open and closed symbols are used for the curves obtained in ZFC and FC modes, respectively.
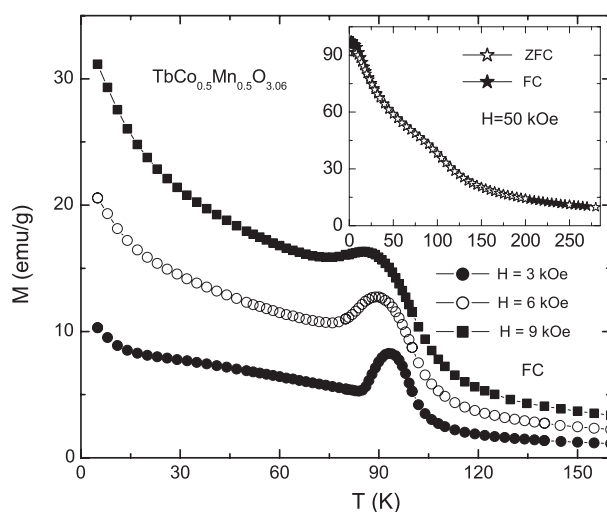

Figure 5. The temperature dependences of magnetization for the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ sample, measured at different magnetic fields.

3.4. Nature of the metamagnetic transitions in LnCo$_{1-x}$Mn$_x$O$_{3+\delta}$

It has been supposed that metamagnetic behaviour in LnCo$_{1-x}$Mn$_x$O$_{3+\delta}$ perovskites is associated with a field-induced transformation of the magnetic structure from ferrimagnetic, where the magnetic moments of Co^{2+} and Mn^{4+} ions are antiparallel, to ferromagnetic, where they are parallel [6]. However, this hypothesis does not conform to the neutron diffraction data, which suggest that Co and Mn in TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ show ferromagnetic coupling. One can assume that metamagnetic behaviour in TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ is due to reorientation of the

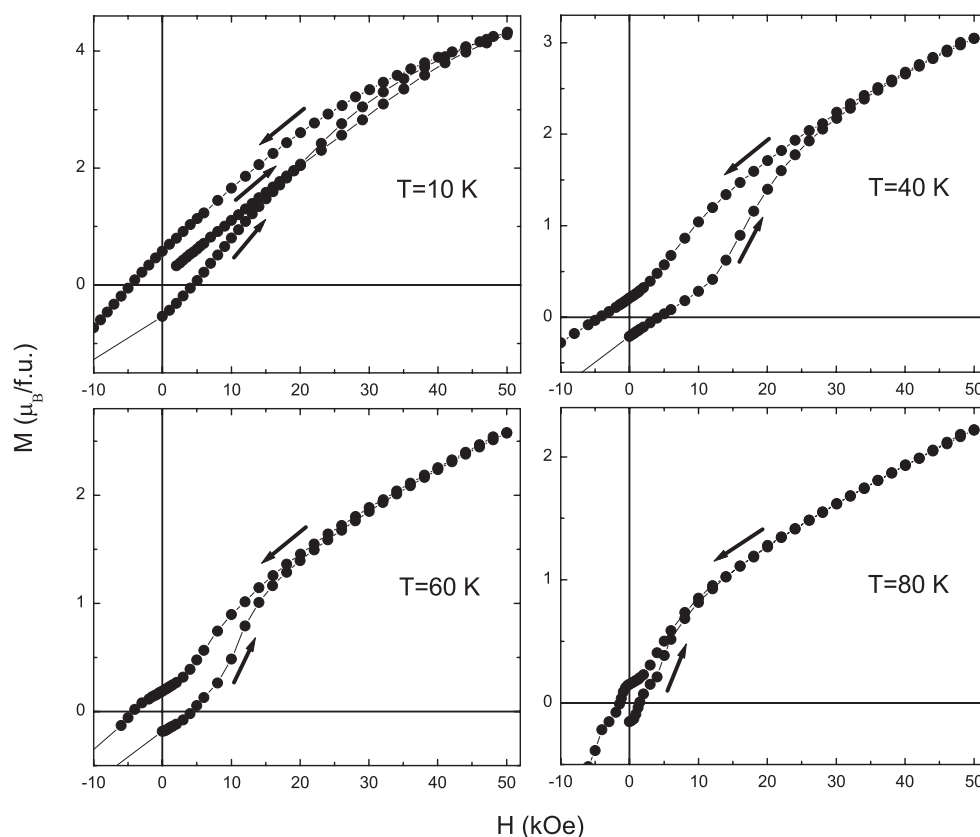**Figure 6.** The field dependences of magnetization for the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ compound at different temperatures.

Tb magnetic moments towards the Co/Mn ones, but the same features of the metamagnetic transitions have been observed for Co-doped manganites with the diamagnetic ions in the A-sublattice (YCo$_{1-x}$Mn$_x$O$_{3+\delta}$) [6].

According to the results of the neutron diffraction experiments, the TbCo$_{0.5}$Mn$_{0.5}$O$_{3.06}$ sample consists of ferromagnetic and spin-glass-like phases. The former has to correspond to the crystallographically ordered clusters with a positive Co^{2+}–O–Mn^{4+} superexchange [1, 2]. In the disordered clusters, competition between the positive Co^{2+}–O–Mn^{4+} and negative Co^{2+}–O–Co^{2+} and Mn^{4+}–O–Mn^{4+} interactions as well as the presence of diamagnetic Co^{3+} ions leads to the formation of the spin-glass-like state [17]. Neutron diffraction data show that the spin-glass-like phase transforms into the ferromagnetic phase under an external magnetic field, therefore we believe that metamagnetic transitions illustrate the development of long-range ferromagnetic ordering from short-range antiferromagnetic ordering.

Acknowledgments

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