

Influence of the Grain Size on the Magnetic Properties of TbMnO₃

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The magnetic properties including magnetic structure of poly and nano samples of TbMnO₃ are determined. All the samples investigated are antiferromagnets. In these samples the Mn and Tb moments order antiferromagnetically at different temperatures and form modulated magnetic structure described by the propagation vector $\mathbf{k}=(k_x,0,0)$ with different value of k_x for the Mn and Tb sublattices. Comparison of the data for poly and nano samples indicates the decrease of the moment and increase of the k_x component of propagation vector in the nano specimens. The wide Bragg peak related to the Tb sublattice suggests that the magnetic order has the cluster-like character. The magnetic moments value in both sublattices is smaller, whereas the k_x values are larger for nano samples.

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1. Introduction

TbMnO₃ compound has been attracting a lot of attention in the last years because of its strong coupling between magnetism and ferroelectrics [1–3]. This compound crystallizes in the orthorhombic distorted perovskite structure (space group *Pnma*). The magnetic data indicate that the Tb and Mn moments order at temperatures near 7 and 40 K, respectively [4]. Neutron diffraction data for the poly and single crystal indicate that the magnetic order in both sublattice is described by the propagation vector $\mathbf{k}=(k_x, 0, 0)$ with the $k_x \approx 0.29$ and 0.43 for the Mn and Tb sublattices, respectively [4–6]. Analysis of the intensity of the peaks of the magnetic origin gives contrary result concerning these orders. Most probably model is following:

- the Mn moments form collinear structure over the temperature range 21 K — T_N and noncollinear at low temperatures,

- the Tb moments form noncollinear structure at low temperatures,
- below 28 K the electric polarization was observed [1].

In last years the properties of nano particle are a subject of intensive investigations. These investigations aim to determine the influence of the crystallites sizes and/or surface-to-volume ratio on magnetic properties.

This work reports the results of the magnetic and neutron diffraction measurements to determine magnetic properties of TbMnO₃ including the magnetic structure of poly as reference sample and nano samples synthesized with a sol-gel method at temperatures of 800 and 850 °C.

2. Experimental details and results

The poly and nano TbMnO₃ samples were prepared by using the co-precipitation technology. The X-ray powder diffraction data at room temperature indicate that all the samples have the orthorhombic crystal structure (space group *Pnma*). The grain size equal of 45 and 60 nm for samples from 800 to 850 °C was estimated with both BET's method and X-ray diffraction measurements [7].

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The dc magnetic measurements were carried out using of commercial MPMS SQUID magnetometer in the magnetic fields up to 50 kOe in the temperature range 2–300 K. Powder diffraction patterns were collected using the E2 ($\lambda = 2.40 \text{ \AA}$) for poly and E6 ($\lambda = 2.447 \text{ \AA}$) for nano samples diffractometer installed at the BERII reactor (Helmholtz-Zentrum-Berlin) within the temperature range from 1.6 to 260 K. The neutron diffraction data were analyzed using the Rietveld-type program FullProf [8].

Analysis of the neutron diffraction patterns measured at different temperatures confirms that the orthorhombic structure is stable in all investigated region of temperature (see Fig. 1). The distribution of atoms is described by the $Pnma$ space group in which Tb and O1 atom occupy the 4(c) site: $x, 1/4, z$; Mn atoms — the 4(b) site: $0, 0, 1/2$ and O2 atoms — the 8(d) site: x, y, z . The temperature dependence of the lattice a , b and c parameters and unit cell volume V for the polycrystalline samples is shown in Fig. 2. All parameters have minimum at $T = 30 \text{ K}$ and quickly increase with increasing temperature.

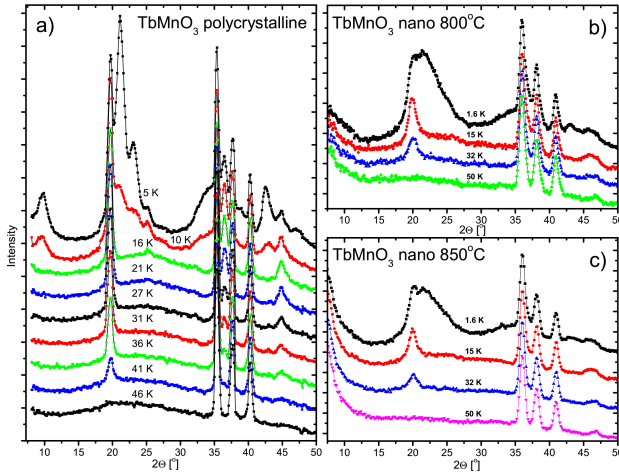


Fig. 1. The low angle neutron diffraction patterns observed at different temperatures for TbMnO_3 : (a) poly ($\lambda = 2.4 \text{ \AA}$) and (b) and (c) nano samples obtained at 800 and 850 °C, respectively ($\lambda = 2.447 \text{ \AA}$).

The data for the nano-samples indicate that a -constant is smaller and b and c are higher than ones for poly sample.

The atomic positional parameter of Tb, O1 and O2 atoms does not change in all the samples [9].

Figure 3 shows the temperature dependence of the magnetic susceptibility at low temperatures. The maxima at 9 K for polycrystalline sample and at 6.7 K for both nano samples are observed. According to the neutron diffraction data, these maxima are connected with ordering in the Tb sublattice. The maxima for nano samples have the broad character which suggests the cluster-like character of the magnetic order in this sublattice. In the temperature range 50–300 K the reciprocal magnetic

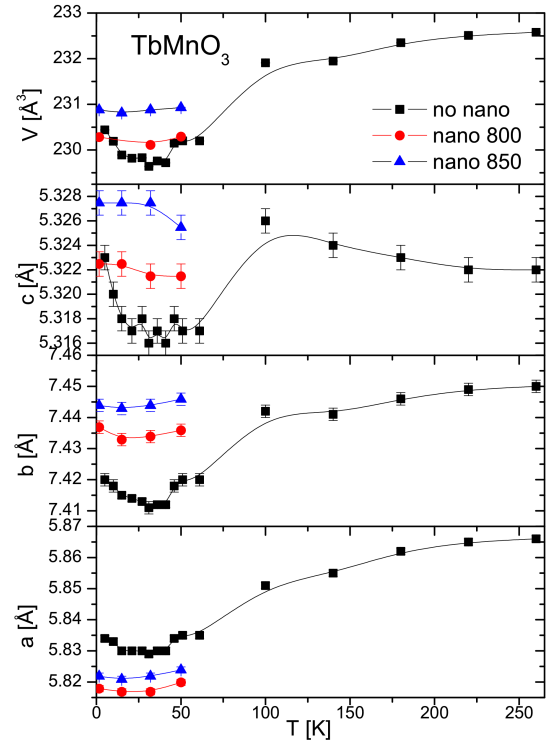


Fig. 2. Temperature dependence of the lattice a , b and c parameters and unit cell volume V for poly and nano samples of TbMnO_3 .

susceptibilities obey the Curie–Weiss law. The values of the paramagnetic Curie temperature θ_p and the effective magnetic moments μ_{eff} are summarized in Table I. The negative values of θ_p suggest that the antiferromagnetic interactions are dominated. The values of μ_{eff} for nano samples are smaller than for poly.

The neutron diffraction patterns at low temperatures (see Fig. 1) suggest the additional peaks connected with the magnetic origin. These peaks can be indexed by propagation vector $\mathbf{k} = (k_x, 0, 0)$. The temperature dependence of k_x component connected with the Mn sublattice for poly sample is shown in Fig. 4. The value of k_x is constant in temperature range 5–30 K and increases near T_N . Numerical analysis of the intensities of magnetic peak indicate that the magnetic order in the Mn sublattice is described by the C_x -mode (see Appendix) in the temperature range 21–41 K. The Mn-moments are parallel to the a -axis and form a collinear incommensurate structure with the crystal structure one.

At $T = 16 \text{ K}$ the additional peaks ($2\theta = 26^\circ$) (Fig. 1a) corresponding to A -mode are observed. The new order is noncollinear with the Mn moments in the a - c plane described by the $C_x A_z$ mode. Temperature dependence of the Mn moment gives the Néel temperature equal to 43 K.

At $T = 5 \text{ K}$ the additional peaks connected with the ordering of the Tb moments are observed (see Fig. 1a). The position of these peaks are described by the prop-

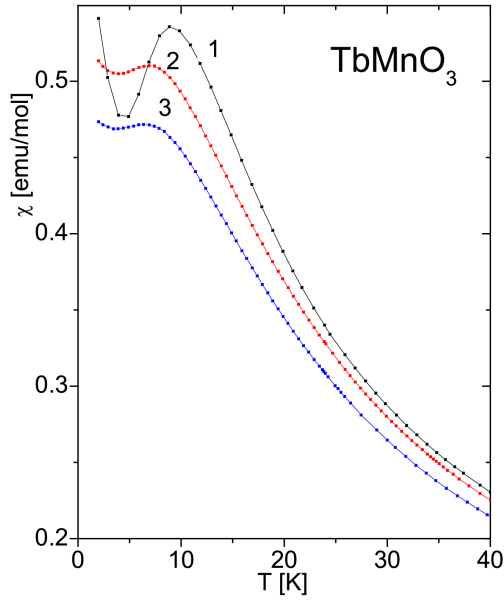


Fig. 3. Temperature dependence of the magnetic susceptibility for poly (1) and nano (2 and 3) samples obtained at 800 and 850 °C.

TABLE I

Magnetic data for TbMnO_3 .

sample	T_N [K]	θ_p [K]	$\mu_{\text{eff}} (\mu_B)$
Poly	9.0	-26.5	10.9(5)
Nano 800	6.7	-29.0	10.6(1)
Nano 850 °C	6.7	-30.0	10.7(1)

T_N — Néel temperature, θ_p — paramagnetic Curie temperature, μ_{eff} — effective magnetic moment. Theoretical value calculated from relation $\mu_{\text{eff}} = \sqrt{(\mu_{\text{eff}}^{\text{Tb}})^2 + (\mu_{\text{eff}}^{\text{Mn}})^2}$ for $\mu_{\text{eff}} = 9.72\mu_B$ (Tb^{3+}) and $4.90\mu_B$ (Mn^{3+}) is equal to $10.88\mu_B$.

agation vector $\mathbf{k} = (0.423(1), 0, 0)$. The magnetic order is noncollinear described by the $A_x F_y C_z$ mode and the total magnetic moment is equal to $6.7(1)\mu_B$.

Analysis of neutron diffraction patterns for nano samples indicates that at temperatures 1.6, 15 and 32 K (see Figs. 1b and c) the Mn-moments form the collinear incommensurate structure described by the C_x mode. This magnetic order is stable up to 1.6 K. At 1.6 K the additional peaks connected with the Tb moments and described by the $A_x C_z$ mode are observed. The peaks corresponding of this order are widening. The magnetic moments values in the Mn and Tb sublattices and corresponding values of the k_x components of the propagation vector are listed in Table II.

3. Concluding remarks

All compounds crystallize in the orthorhombic crystal structure described by the space group $Pnma$. The value

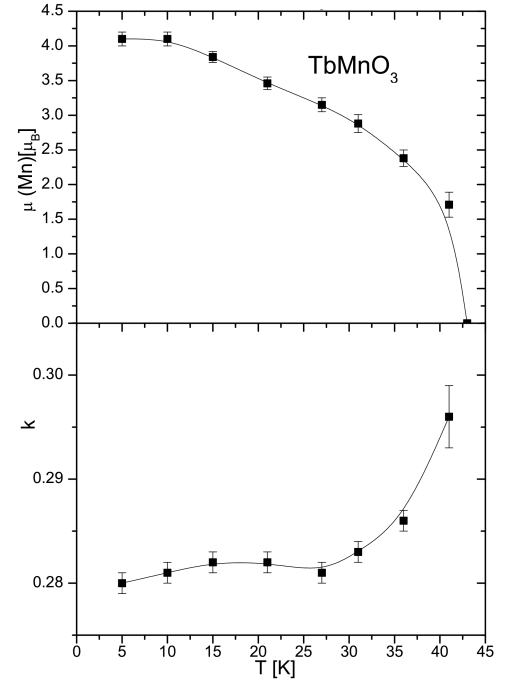


Fig. 4. Temperature dependence of the k_x component of the propagation vector \mathbf{k} for the Mn sublattice and values of the Mn magnetic moment for poly sample.

TABLE II

Parameters of the magnetic structure for nano-800 and nano-850 samples of TbMnO_3 .

T [K]	nano-800			nano-850		
	$\mu_{\text{Mn}} [\mu_B]$	k_y	R_m [%]	$\mu_{\text{Mn}} [\mu_B]$	k_y	R_m [%]
32	1.60(12)	0.326(4)	19.2	1.35(15)	0.326(5)	20.9
15	2.29(8)	0.312(2)	11.5	2.08(10)	0.315(2)	19.1
1.6	2.94(2)	0.321(2)	10.9	3.03(4)	0.328(2)	13.1
X	3.68(11)	0.443(5)	9.2	4.43(7)	0.451(3)	9.3

X — $\mu_{\text{Tb}}^* [\mu_B]$ data for the Tb sublattice at 1.6 K.

of the lattice parameters indicates the small influence of the grain size on atomic ordering.

Comparison the magnetic and neutron diffraction data for poly and nano samples indicate the following difference:

- the Néel temperature T_N connected with the Tb sublattice are lower for nano samples,
- the broad maximum at T_N and wide magnetic peaks suggest that the ordering in the Tb sublattices has the cluster-like character,
- in polycrystalline sample the change of ordering in the Mn-sublattice from collinear to noncollinear with decreasing temperature is observed while in nanoparticle samples a collinear ordering is stable up to 1.6 K,

- the effective magnetic moment of Mn^{3+} and Tb^{3+} in the ordered state are smaller for nano samples,
- the values of k_x component for both (Mn and Tb) sublattices are larger for nano samples.

Observed decrease of the effective moment seems to be connected with rise of the Mn^{4+} concentration [10], when the ordered moment can be explained by spin disorder in a surface shell of nanogranular systems as proposed in Ref. [11].

The inelastic neutron scattering for TbMnO_3 yields the positive value ($J' \approx 0.15(1)$ meV) of the exchange integral in the a - c plane and negative value ($J'' \approx -0.31(2)$ meV) of the exchange integral along the b -axis [12]. Analysis of the interactions for this compound gives the following dependence between k_x and the exchange integrals — $\cos(\pi k_x) \approx (2J'' - J')$ [13]. Increase of the k_x component indicates the decrease of the exchange integrals. Results presented in the work suggest increase of the exchange integrals in nano samples, which confirms a reduction of the Néel temperature observed in Tb sublattice.

4. Appendix

In this appendix we will discuss the possible magnetic structures compatible with the crystal symmetry, obtained through the group theory analysis following the method described by Bertaut [14]. The magnetic modes are given by the basis vectors of the irreducible representations of the little group G_k , which is formed by those elements of the space group $Pnma$.

In TbMnO_3 (space group $Pnma$) the Mn^{3+} ions in the $4b$ site can be described by four Bravais lattices labeled as: $\text{Mn}_1(0, 0, 1/2)$, $\text{Mn}_2(1/2, 0, 0)$, $\text{Mn}_3(0, 1/2, 1/2)$ and $\text{Mn}_4(1/2, 1/2, 0)$ where Tb^{3+} ions in $4(c)$: $\text{Tb}_1(x, 1/4, z)$, $\text{Tb}_2(1/2 - x, 3/4, 1/2 + z)$, $\text{Tb}_3(x, 3/4, z)$ and $\text{Tb}_4(1/2 + x, 1/4, 1/2 - z)$.

Therefore, four modes are possible, namely, one ferromagnetic arrangement: $F = m_1 + m_2 + m_3 + m_4$ and three antiferromagnetic arrangements: $A = m_1 - m_2 - m_3 + m_4$, $C = m_1 + m_2 - m_3 - m_4$ and $G = m_1 - m_2 + m_3 - m_4$ can be distinguished [14].

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References

- [1] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, *Nature* **426**, 55 (2003).
- [2] M. Kenzelmann, A.B. Hari, S. Jones, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.-W. Cheong, O.P. Vajk, J.W. Lynn, *Phys. Rev. Lett.* **95**, 087206 (2005).
- [3] M. Mostovoy, *Phys. Rev. Lett.* **96**, 067601 (2006).
- [4] S. Quezel, F. Tcheou, J. Rossat-Mignod, G. Quezel, E. Roudaut, *Physica B* **86-88**, 916 (1977).
- [5] R. Kajimoto, H. Yoshizawa, H. Shintani, T. Kimura, Y. Tokura, *Phys. Rev. B* **70**, 012401 (2004).
- [6] O. Prokhnenko, R. Feyerherm, M. Mostowoy, N. Aliouane, E. Dudzik, A.U.B. Wolter, A. Maljuk, D.N. Argyrion, *Phys. Rev. Lett.* **99**, 177206 (2007).
- [7] V. Dyakonov, A. Szytula, R. Szymczak, E. Zubov, A. Szewczyk, Z. Kravchenko, W. Bažela, K. Dyakonov, A. Zarzycki, V. Varyukin, H. Szymczak, *Low Temp. Phys.* **38**, 1 (2012).
- [8] J. Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).
- [9] W. Bažela, M. Dul, V. Dyakonov, Ł. Gondek, A. Hoser, J.-U. Hoffmann, B. Penc, A. Szytula, Z. Kravchenko, I. Nosalev, A. Zarzycki, *J. Magn. Mater.* in press.
- [10] T.I. Arbutova, B.A. Gizhevski, R.G. Zakharov, S.A. Petrova, N.M. Chebotaeve, *Phys. Solid State* **50**, 1487 (2008).
- [11] M.A. Lopez-Quintela, L.E. Heuso, J. Rivas, F. Rivadulla, *Nanotechnology* **14**, 212 (2003).
- [12] D. Senff, P. Link, K. Hradil, A. Hiess, L.P. Regnault, Y. Sidis, N. Aliouane, D.N. Argyrion, M. Braden, *Phys. Rev. Lett.* **98**, 137206 (2007).
- [13] H.W. Brinks, J. Rodriguez-Carvajal, H. Fjellvåg, A. Kjekshus, B.C. Hauback, *Phys. Rev. B* **63**, 094411 (2001).
- [14] E.F. Bertaut, in: *Magnetism*, Vol. III, Eds. G.T. Rado, H. Shul, Academic Press, N.Y. 1963, p. 149.