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Praca doktorska:

Badanie wpływu rozmiarów ziaren na strukturę krystaliczną i własności magnetyczne nanozwiązków typu $REMnO_3$ (RE = Tb, Dy)

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Summary of the Doctoral Thesis

Title: **Influence of the grain size on the crystal structure and the magnetic properties of the nanoparticle $REMnO_3$ compounds (RE = Tb, Dy)**.

The key part of the dissertation was investigation of the grain size effect on the crystal structure and magnetic properties of the polycrystalline and nanoparticle $REMnO_3$ (RE = Tb, Dy) manganites.

The polycrystalline $REMnO_3$ (Tb, Dy) manganites were prepared by the solid - state reaction and were annealed at 1150°C. For preparation of the nanosize $REMnO_3$ manganites the sol - gel method has been used. The three $TbMnO_3$ nano - samples and the three $DyMnO_3$ nanopowder samples were obtained after annealing at 800°C, 850°C, 900°C and 800°C, 850°C, 900°C, respectively.

The analysis presented in the dissertation was based on the neutron diffraction powder data collected using the E2 and E6 diffractometers installed at the BERII reactor (Helmholtz - Zentrum Berlin) within the temperature range of 1,6 K to 260 K and X - ray powder diffraction data at room temperature using the Philips PW - 3710 X'PERT diffractometer with CuK_α radiation.

The obtained data were analyzed with the Rietveld - type refinement using the Fullprof program.

The X - ray and neutron diffraction data indicate that all the samples studied have orthorhombically distorted perovskite crystal structure (space group *Pnma*, No. 62). In this structure RE and O1 atoms occupy 4(c) site: (x, ¼, z), O2 atoms are in 8(d) site: (x, y, z) and Mn atoms are in 4(b) site: (0, 0, ½).

The grain sizes of the $TbMnO_3$ and $DyMnO_3$ nano - samples were determined using the Scherrer relation and the Williamson - Hall method. The average grain size determined are equal to 62 nm, 56 nm and 60 nm for the $TbMnO_3$ nano - samples after annealing at 800°C, 850°C and 900°C, respectively. The average particle sizes of the $DyMnO_3$ nano - samples obtained after annealing at 800°C, 850°C and 900°C are equal to 77 nm, 67 nm and 78 nm. Presented data indicate that the grain size value increases with increasing annealing temperature.

The magnetic measurements of the nanosize $DyMnO_3$ samples using the MPMS SQUID magnetometer have been carried out: magnetic susceptibility was measured in a magnetic field of 1 kOe over a temperature range of 2 - 300 K (from these data the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p were determined) and magnetization was measured in a magnetic field up to 50 kOe and at temperatures down to 2 K.

All the samples measured are antiferromagnets, in which the Nèel temperature corresponding to the Dy sublattice decreases as the particle size is reduced. Above 50 K, the reciprocal magnetic susceptibility obeys the Curie - Weiss law. The M(T) dependences presented at low temperatures clearly show the anomalies corresponding to the Dy magnetic moment ordering. The values of the effective magnetic moment μ_{eff} suggest that the magnetic moment is localized on the Dy and Mn atoms.

Low - temperature neutron diffraction data indicate that the magnetic ordering of Mn and Tb sublattice for polycrystalline $TbMnO_3$ is sinusoidally modulated described by the propagation vector $\mathbf{k} = (k_x, 0, 0)$. The magnetic moments in Mn sublattice order below 41 K, while the magnetic moments in Tb sublattice order below 9 K.

In the crystal unit cell (space group *Pnma*) the Mn^{3+} and Tb^{3+} sublattices can be described by four modes proposed by Bertaut: one ferromagnetic ordering: $\mathbf{F} = m_1 + m_2 + m_3 + m_4$ and three antiferromagnetic arrangements: $\mathbf{A} = m_1 - m_2 - m_3 + m_4$, $\mathbf{C} = m_1 + m_2 - m_3 - m_4$ and $\mathbf{G} = m_1 - m_2 + m_3 - m_4$.

The Mn magnetic moments, parallel to the *a* - axis, form a collinear incommensurate structure of $\mathbf{C_x}$ - mode. At T = 16 K, a noncollinear magnetic structure described by

$\mathbf{C_xA_z}$ - mode with the Mn moment in the *a* - *c* plane was observed. The Tb sublattice exhibits the antiferromagnetic incommensurate ordering of the $\mathbf{F_yA_z}$ - type at T = 5 K. The Tb magnetic structure is described by the propagation vector $\mathbf{k} = (k_x, 0, 0)$ where k_x is equal to 0,423(1). At the same temperature, the Mn moments still form the $\mathbf{C_xA_z}$ structure described by propagation vector $\mathbf{k} = (k_x, 0, 0)$ where k_x is equal to 0,282(1).

Below T_N, in the nano-800 and nano-850 samples the Mn moments form a collinear incommensurate magnetic structure of $\mathbf{C_x}$ - type described by the propagation vector $\mathbf{k} = (k_x, 0, 0)$.

Magnetic structures of the polycrystalline and nanoparticle $TbMnO_3$ compounds are incommensurate in comparison with the crystal structure. The periods of modulation of the magnetic structure are equal to 3,54*a* (Mn sublattice) and 2,36*a* (Tb sublattice) for the polycrystalline sample and 3,06*a* (Mn) and 2,25*a* (Tb) for the nano - samples.

The $TbMnO_3$ nanosamples are also antiferromagnets. The grain size is established to influence slightly on the Nèel temperature value and sine modulated magnetic ordering. In the case of $TbMnO_3$, an increase of the k_x components value for both sublattices (Mn and Tb) is detected. The peaks corresponding to the magnetic order in Tb^{3+} sublattice are broadening which suggest the cluster - like character of the magnetic ordering in the Tb sublattice.

In order to explain these differences, the detail analysis of the internal structural parameters determined from the X - ray and neutron diffraction data has been performed.

In the orthorhombic unit cell there are the three crystallographically independent bond lengths: apical Mn - O1 (4c) = r_1, and two equatorial Mn - O2 $(8d)_1 = r_2$ and Mn - O2 $(8d)_2 = r_3$ and the two bond angles: (Mn - O1 - Mn) = α and (Mn - O2 - Mn) = β. The temperature dependences of the Mn - O bond lengths and Mn - O - Mn bond angles for the polycrystalline and two nanoparticle $TbMnO_3$ samples were obtained.

Observed antiferromagnetic ordering in the Mn sublattice is result of the superexchange mechanism (cation - anion - cation) which exists in manganites. The superexchange interaction depends on the Mn - O - Mn bond angles (α, β) and is joined with partial overlap of the p(O) and d(Mn) orbitals. For the $TbMnO_3$ manganite the superexchange interaction between Mn - O2 - Mn spins in the *a* - *c* plane (J_1) is ferromagnetic, while the interaction between Mn - O1 - Mn along the *b* - axis is antiferromagnetic (J_2). The values of Mn - O2 - Mn bond angles for polycrystalline and nanosize samples are similar and have an anomalies at the T_N temperature. The values of Mn - O1 - Mn bond angles are higher for the nanoparticle samples. This fact suggests an increase of the superexchange interaction. Above data suggest that a decrease of the grain size results in an increase of the antiferromagnetic interactions along the *b* - axis.

The inelastic neutron scattering for the $TbMnO_3$ poly-sample gives the positive value (J_1 = 0,15(1) meV) of exchange integral in the *a* - *c* plane and the negative value (J_2 = - 0,31(2) meV) of exchange integral along the *b* - axis [Senff D et al.]. These results confirm that for the $TbMnO_3$ manganite the superexchange interaction between Mn - O2 - Mn spins in the *a* - *c* plane (J_1) is ferromagnetic, while the interaction between Mn - O1 - Mn along the *b* - axis is antiferromagnetic (J_2).

The influence of deformation of the MnO_6 octahedron on the magnetic structure of the $TbMnO_3$ manganite is observed. The changes of both the Jahn - Teller effect and the delta parameter is a result of the MnO_6 octahedron distortion. The obtained values of the Jahn - Teller effect and the delta parameter determined by the MnO_6 octahedron distortion as well as the D parameter determined by deformation of the unit cell are much smaller in the nanocrystalline samples than in the polycrystalline ones.

The presented results suggest that the nanoparticle size and local microstructure play an important role in the formation of magnetic properties.