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Neutron Diffraction Studies of Nanoparticle $DyMnO_3$ Compound

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The neutron powder diffraction (NPD) measurements of the nano-size $DyMnO_3$ manganite have been performed. The obtained results indicate that this compound crystallizes in the orthorhombic crystal structure described by the space group *Pnma*. The Mn and Dy moments order antiferromagnetically at different temperatures and form modulated magnetic structure described by the propagation vector $\boldsymbol{k} = (k_x, 0, 0)$ with the different values of k_x component for the Mn and Dy sublattices. The values of k_x component for Mn sublattice increase with decreasing of the temperature and are smaller that in bulk compound. The wide Bragg peaks related to the Dy sublattice suggest that the magnetic order in this sublattice has the cluster-like character.

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1. Introduction

The family of perovskite-like oxides $RMnO_3$, where R are rare earth elements, has been extensively studied in recent years. These investigations concentrate also on the influence of grain size on the magnetic properties. The neutron diffraction data for $DyMnO_3$ compounds indicates the change of the parameters of the magnetic ordering with the change of the grain size [1].

This work reports the results of the neutron diffraction measurements for the isostructural $DyMnO_3$ nanoparticle compound. At room temperature, the bulk $DyMnO_3$ compound exhibits the orthorhombically distorted perovskite structure (space group *Pnma*). The magnetic moments in particularly sublattices are order in different temperatures: at 39 K for Mn and 6.5 K for Dy sublattices. At low temperatures the magnetic moments in both sublattices form sine-modulated structure described by the propagation vector $\boldsymbol{k} = (k_x, 0, 0)$ with k_x equal to 0.405 for Mn site and 0.5 for Dy site [2].

Investigated in this work sample of nanosize $DyMnO_3$ manganite is prepared by the sol–gel method described in Ref. [3]. The X-ray data at room temperature indicate that the sample has orthorhombic structure. The grain size was determined using the Scherrer relation $d = (\lambda/B)\cos\theta_B$, where d is the grain size, $\lambda = 1.5418$ Å — the X-ray wavelength, θ_B — the corresponding angle of the Bragg diffraction and B the difference between half-widths of the Bragg reflex of the nanopowder and the standard sample Si with the size grain equal to 10 μm. For the sample annealed at 850 °C the average size grain is 48 nm. The magnetic data indicate the Néel temperature for Dy sublattice equal to 8.3 K. In this work in purpose to explain microscopic properties concerning the crystal and magnetic structure of nanoparticle sample $DyMnO_3$ the neutron diffraction experiment is reported.

2. Experimental details and results

The neutron diffraction experiment has been performed on the sample which was obtained by the sol–gel method and next annealed at 850 °C [3]. The neutron diffractograms were obtained at temperatures equal to 1.6, 12, 25, and 50 K with the use of the E6 diffractometer at BERII reactor (Helmholtz–Zentrum Berlin). The incident neutron wavelength was 2.44 Å. The data were analyzed using the Rietveld-type program FullProf [4].

TABLE

Crystal structure parameters of nanosized $DyMnO_3$ compound refined on the basis of the neutron diffraction patterns collected at 1.5 and 50 K. Standard deviations are given in parentheses.

Parameters/T [K]	1.5	50
a [Å]	5.8265(8)	5.8267(9)
b [Å]	7.3621(12)	7.3661(13)
c [Å]	5.2762(8)	5.2793(9)
V [Å^3]	226.32(11)	226.59(11)
x_{Dy}	0.0833(7)	0.0845(8)
z_{Dy}	0.9846(9)	0.9823(11)
x_{O1}	0.4652(15)	0.4611(20)
z_{O1}	0.1122(18)	0.1164(22)
x_{O2}	0.3302(15)	0.3342(17)
y_{O2}	0.0507(10)	0.0527(11)
z_{O2}	0.7006(16)	0.7043(20)
R_{Bragg} [%]	4.40	4.62
$R_{prof.}$ [%]	3.57	3.55

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The neutron diffraction patterns measured at different temperatures are shown in Fig. 1. The data confirm that investigated compound crystallizes in the orthorhombic crystal structure (space group *Pnma*) with the following distribution of atoms: the Dy and O1 atoms occupy the 4(c) site: x, 1/4, z; the Mn atom 4(b) site: 0, 0, 1/2 while O2 atoms in the 8(d) one: x, y, z. The crystal structure parameters determined from the data at 1.5 and 50 K are listed in Table. The analysis of these data indicates that the orthorhombic crystal structure is stable down to low temperatures.

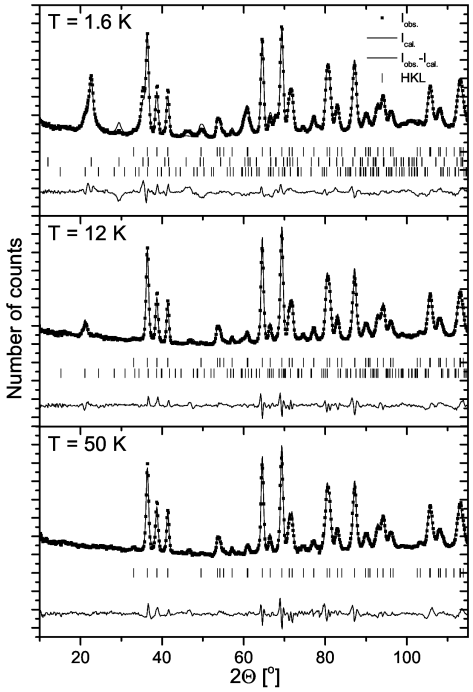

Fig. 1. Comparison between the observed and calculated NPD patterns by the Rietveld method at (a) 1.6 K, (b) 12 K, and (c) 50 K. The symbols represent the experimental data while the solid line denotes the calculated profile. The difference between the observed and calculated intensities is shown at the bottom of each diagram. The vertical bars indicate the positions of the Bragg peaks, first row nuclear, second and third magnetic connected with the Mn- and Dy-sublattices.

On the neutron diffraction patterns at 1.6, 12, and 25 K the additional peaks connected with the magnetic origin are observed. These peaks can be indexed by propagation vector $\boldsymbol{k} = (k_x, 0, 0)$. The values of k_x components which described the ordering in Mn site are equal to 0.360(4), 0.370(2), and 0.376(4) at 25, 12, and 1.6 K, respectively.

In crystal unit cell the Mn^{3+} ions in the 4(b) site can be described by four Bravais lattices labeled as: Mn1 $(0, 0, 1/2)$, Mn2 $(1/2, 0, 0)$, Mn3 $(0, 1/2, 1/2)$, and Mn4 $(1/2, 1/2, 0)$ where Dy^{3+} ions in 4(c): Dy1 $(x, 1/4, z)$, Dy2 $(1/2 - x,\ 3/4,\ 1/2 + z)$, Dy3 $(\bar{x}, 3/4, \bar{z})$ and Dy4 $(1/2+x,\ 1/4,\ 1/2-z)$. The analysis based on the Bertaut method [5] provides four modes: one ferromagnetic: $\boldsymbol{F} = m_1 + m_2 + m_3 + m_4$ and three antiferromagnetic ones: $\boldsymbol{A} = m_1 - m_2 - m_3 + m_4$, $\boldsymbol{C} = m_1 + m_2 - m_3 - m_4$, and $\boldsymbol{G} = m_1 - m_2 + m_3 - m_4$. Numerical analyses of the intensities of magnetic peak indicate that the magnetic ordering in the Mn sublattice is described by the A_x mode. This magnetic order is stable up to 1.6 K. The Mn-moments are parallel to the a-axis and form a collinear incommensurate structure with the crystal structure one. The magnetic moments localized on the Mn atoms are equal to 3.24(14), 3.74(12) and 4.24(11) μ_B at 25.12 and 1.6 K, respectively. The magnetic R-factors are equal to 11.7, 9.9, and 10.1%, respectively.

At $T = 1.6$ K the additional peaks corresponding to the magnetic ordering in Dy sublattice described by the A_x-mode are observed. The magnetic order is described by the propagation vector $\boldsymbol{k} = (0.501(12), 0, 0)$. The Dy moments equal to 8.71(18) μ_B are parallel to the a-axis ($R_{mag} = 10.0\%$).

3. Conclusions

Presented in the work data indicate that the nanoparticle sample of $DyMnO_3$ crystallizes in the orthorhombic crystal structure described by the space group *Pnma* similar to those for bulk material. The values of the structural parameters indicate the small influence of the grain size on atomic ordering.

Comparison of the data for nano and bulk samples suggest that the ordering in the Mn and Dy sublattices described by the propagation vector $\boldsymbol{k} = (k_x, 0, 0)$ is similar. For a nanosample the values of the k_x components for the Mn sublattice are smaller that for bulk material and indicate the incommensurate structure while for Dy sublattice similar as in bulk compound and corresponding to the commensurate one. The wide Bragg peaks related to the Dy sublattice suggests that magnetic order has the cluster-like character. Similar effect is observed in the isostructural nano $DyMnO_3$ compound [1]. The value of the Mn magnetic moment is near the value for the Mn^{3+} ions (4.0 μ_B corresponding to $S = 2$) while this for Dy moments is smaller that for Dy^{3+} ion (10.0 μ_B) which suggests the influence of the crystal electric field.

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