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# Magnetic and magnetotransport properties of nickel-doped manganites

**Abstract.** *Structural and magnetization measurements have been performed on the $La_{1-x}Sr_xMn_{0.5}Ni_{0.5}O_3$ ($0 \leq x \leq 0.2$) with perovskite structure. Structural data testify a partial order of the Ni and Mn ions in all the compounds in spite of chemical substitution of the $La^{3+}$ ions by $Sr^{2+}$ ones and an increase of the oxidation state of the Ni ions from 2+ towards to 3+ one. Magnetic structure of the compounds changes from ferromagnetic one to antiferromagnetic (compounds with $x \geq 0.1$) while the temperature of a transition into paramagnetic state remains about 270 K for all the samples.*

**Streszczenie.** *Wykonano strukturalne i magnetyzacyjne pomiary na $La_{1-x}SrxMn_{0.5}Ni_{0.5}O_3$ ($0 \leq x \leq 0.2$) ze strukturą perowskitu. Dane strukturalne potwierdzają częściowe uporządkowanie jonów Ni i Mn we wszystkich związkach pomimo chemicznej substytucji jonów $La^3+$przez jony $Sr^2+$ oraz zwiększenia stanu utlenienia jonów Ni od 2+ do 3+. Struktura magnetyczna związków zmienia się ze stanu ferromagnetycznego do antyferromagnetycznego (związki o $x \geq 0.1$), podczas gdy temperatura przejścia w stan paramagnetyczny pozostaje w przybliżeniu stał dla wyrzyskich próbek i wynosi 270 K.* **(Właściwości magnetyczne i magnetotyczne manganitów domieszkowanych niklem).**

**Keywords:** Magnetic materials, diffraction, magnetoresistive effect, exchange interaction.
**Słowa kluczowe:** Materiały magnetyczne, dyfrakcja, efekt magnetorezystywny, interakcje wymiany.

## Introduction

Solid solutions of manganese, nickel and cobalt with perovskite structure are the model objects to study magnetic properties of transition metal oxides demonstrating intriguing properties which often remain to be unexplained. Ferromagnetism of manganites and cobaltites materials as well as their metallic type conductivity can be induced by chemical substitution of $La^{3+}$ ions by $Sr^{2+}$ ones resulted in heterovalent Mn and/or Co ions in related solid solutions as $La_{1-x}^{3+}Sr_x^{2+}Mn(Co)O_3$ [1-4]. There is another way to get dielectric ferromagnetic state of manganites – via chemical substitution of $Mn^{3+}$ ions by nickel or cobalt ones [5-8]. Maximal values of the Curie points have been observed for the compounds with 50% substitution of the Mn ions which is primarily associated with structural order of Mn and Co(Ni) ions [5-9]. It is known that the synthesis conditions determine the values of the Curie points which can vary significantly, e.g. 280 K for $LaMn_{0.5}Ni_{0.5}O_3$ compound [8, 9] and 230 K for $LaMn_{0.5}Co_{0.5}O_3$ one [6] depending on the structural order of the related ions. It is considered in Ref [10] that transition metal ions are structurally disordered in the compounds having low temperature magnetic transition, structural order of these ions favors higher transition temperature [11]. The recent structural data obtained by XMCD method [6] testify that preferred oxidation state of the transition metal ions are $Mn^{4+}$ and $Ni^{2+}$ ($Co^{2+}$) ones which highlights important role of the structural order of the heterovalent ions. It should be noted that different methods to study structural order show significantly different results, e.g. neutron diffraction study of the compounds with relatively high Curie points testify a well ordered structure formed by heterovalent ions Co, Ni and Mn. While the results of the electron diffraction measurements testify an incommensurate crystal structure only in a few crystallines [12].

Chemical substitution of the $La^{3+}$ ion by $Sr^{2+}$ ones should change the electronic configuration of $Ni^{2+}$ ions towards to $Ni^{3+}$ one assuming constant oxygen stoichiometry of the compounds. It is considered that an appearance of the $Ni^{3+}$ ions should disrupt the charge order. The mentioned approach to substitute Mn ions by other transition metal ions can permit to reveal the effect of the charge order of the Mn and Ni ions on the magnetic properties of the respective compounds as well as to estimate the sign and the magnitude of the superexchange interactions between Ni and Mn ions.

## Experimental

Polycrystalline samples of $La_{1-x}Sr_x(Mn_{0.5}Ni_{0.5})O_3$ ($0 \leq x \leq 0.2$) have been obtained by standard ceramic technology using oxides $La_2O_3$, $Mn_2O_3$, NiO and carbonate $SrCO_3$ of high purity. The oxide $La_2O_3$ was annealed at 1050°C to remove humidity. The oxides taken in stoichiometric ratio were thoroughly mixed in planetary mill RETSCH PM 100. Preliminary annealing was performed at 1100°C for 5 hours and the obtained product was thoroughly ground. A final synthesis was performed in air at temperature of 1420°C for 7 hours followed by gradual temperature decrease down to 300°C during 12 hours. Phase purity has been estimated using step-scanned X-ray diffraction data collected at room temperature using a DRON-3M diffractometer with Cu-$K_\alpha$ radiation. Neutron diffraction data were collected using the high resolution powder diffractometer E9 at Helmholtz-Zentrum for Materials and Energy (Berlin) with the wavelength of 1.7982 Å. The experimental data were analysed by the Rietveld method using the FullProf software package. Magnetization and magnetoresistance measurements by four-probe method were made using physical properties measurement system (PPMS, Cryogenic Ltd) in magnetic fields up to 14 T. Ultrasonically deposited indium was used for formation of contacts.

## Results and discussion

Analysis of the XRD patterns recorded for the compounds with $0 \leq x \leq 0.15$ did not reveal any impurity phases while the XRD data of the compound with $x = 0.2$ testify an existence of the admixture oxide NiO (~3%). The unit cell parameters of the compounds with $x \leq 0.2$ have been calculated assuming the rhombohedral crystal structure (space group $R-3$). The structural data testify a decrease of the unit cell volume with increase of the $Sr^{2+}$ content. This modification of the crystal structure evidences about an increase in the oxidation state of the nickel ions as the ionic radius of the $La^{3+}$ ions is significantly less than that of $Sr^{2+}$ one and the ionic radius of the $Ni^{3+}$ is notably smaller than that attributed to $Ni^{2+}$ ion.

Figure 1 shows the temperature dependences of the magnetization measured in FC and ZFC modes for the compounds with $x = 0$, 0.1 in weak magnetic fields. The magnetization data testify a ferromagnetic behavior of the compound $LaMn_{0.5}Ni_{0.5}O_3$ with Curie temperature of about 270 K.
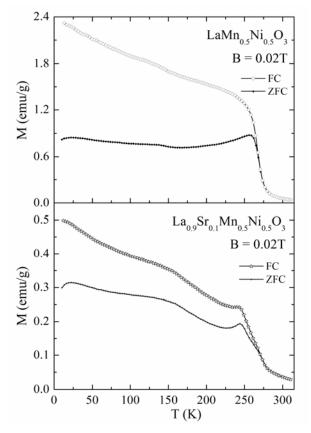


Fig.1. Temperature dependencies of magnetization obtained in FC and ZFC modes for $x=0$ and $x=0.1$ compounds.

The unsaturated magnetization denoted in the strong magnetic fields points at the competition between superexchange interactions of different signs which becomes dominantly antiferromagnetic upon chemical substitution of the $La^{3+}$ ions by the $Sr^{2+}$ ones.
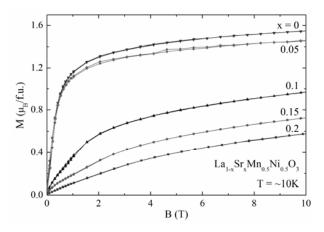


Fig.2. Field dependencies of magnetization for $La_{1-x}Sr_x(Mn_{0.5}Ni_{0.5})O_3$ samples.

Surprisingly, the critical temperature of the magnetic transition remains nearly stable with an increase in strontium content (Fig. 1). The observed behavior is contradicts to the decrease of the spontaneous magnetization observed upon an increase of the $Sr^{2+}$ content. Spontaneous magnetization is nearly nullified in the compounds with $x \geq 0.15$ (Fig. 2).

The conductivity measurements testify a semiconductor behavior of all the compounds under study with resistivity of about $\sim 10^7$-$10^8$ $\Omega \cdot cm$ at low temperatures. We did not observe any anomalies on the conductivity dependencies near the temperature transition to the magnetically ordered state. It should be noted that the magnitude of the magnetoresistance increases upon temperature decrease and diminishes with an increase of strontium content above $x \geq 0.1$ (Fig. 3). There is no magnetoresistance effect at temperatures near the Curie point and we didn't observe a tunnel magnetoresistance effect in the whole measured temperature range unlike the results presented in the Ref. [8]. The observed magnetoresistance behavior can be explained assuming a weak spin polarization of the charge carriers and magnetoresistance effect is most probably associated with the magnetic and structural disorder and strong 3d-2p hybridization of the related orbitals of the manganese and oxygen ions which is strengthened in magnetic field.
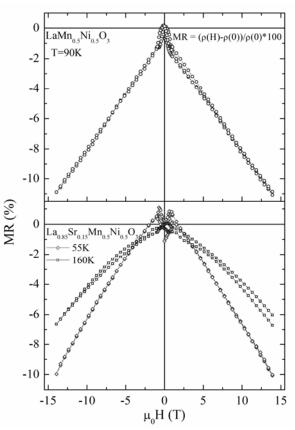


Fig.3. Magnetoresistance vs. magnetic field at different temperatures for $La_{1-x}Sr_xMn_{0.5}Ni_{0.5}O_3$ ($x = 0$; 0.15) samples.

Neutron diffraction measurements for the compounds with $x = 0.1$ and 0.2 have been performed in the temperature range 2-300 K (Fig. 4). The diffraction patterns recorded at 300 K have been successfully refined considering a rhombohedral type of the unit cell distortion. The structural refinement has been performed with space group $R$-$3$ which assumes a chess-like ionic order of the Mn and Ni cations. At temperatures lower than 25 K one can denote a significant increase in the intensity of the diffraction peak indexed as (101)|(100) which involves both structural and magnetic components of neutron scattering. An increase in the intensity of the mentioned peak upon

temperature decrease points at a formation of the antiferromagnetic order of G-type which onset nearly coincides with the anomaly on the magnetization dependence at high temperature and an appearance of the spontaneous magnetization. It should be noted that the discussed reflection is significantly broader than other reflections thus indicating the inhomogeneous distribution of the Ni and Mn ions itself as well as their magnetic moments.
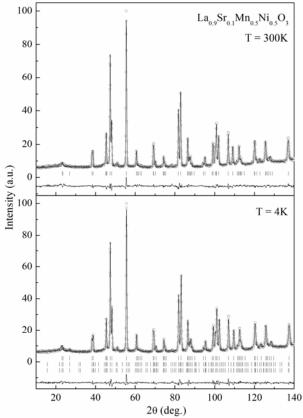


Fig.4. Neutron powder diffraction patterns recorded at 300 K and 2 K for $La_{0.9}Sr_{0.1}Mn_{0.5}Ni_{0.5}O_3$ sample. The black line and red points denote the calculated and observed profiles, respectively. The bottom blue line represents their difference. The row of vertical ticks marks the Bragg reflections of the structural and magnetic phases.

The main parameters of crystal and magnetic structures are denoted in the Table 1. Low values of the reliability factors calculated during the refinement (see Table 1) testify a good correlation between the observed and the calculated parameters which confirms an oxygen stoichiometry and in turn the oxidation states of the Ni and Mn ions to be thus 3+ and 4+ respectively. The calculated value of the magnetic moment at 2 K is about 1.5 $\mu_B$ which is lower than that estimated in case of the homogeneous magnetic structure. The structural parameters calculated for the compound with $x = 0.1$ are quite close to those calculated for the compound $x = 0.2$ while the unit cell volume of the latter compound is slightly smaller while the magnetic moment is slightly larger - 1.7 $\mu_B$.

In order to clarify an evolution of the magnetic properties of the compounds as a function of the chemical substitution of $La^{3+}$ ions by the $Sr^{2+}$ ions one should know the sign and the strength of the superexchange interactions between $3d$ ions. According to the Goodenough-Kanamori rule the interaction between $Mn^{4+}$-O-$Mn^{4+}$ ions always has negative sign as well as that between $Ni^{2+}$-O-$Ni^{2+}$ ions [13]. Therefore, it is considered that ferromagnetism of the compound $LaMn_{0.5}Ni_{0.5}O_3$ is governed by positive exchange interaction between $Ni^{2+}$ and $Mn^{4+}$ ions. While the magnetic

moment estimated for the present compound with $x = 0$ is significantly lower than that calculated assuming pure ionic model.

Table 1. Structural and magnetic parameters (lattice parameters, fractional atomic coordinates and magnetic moments) and reliability factors calculated for $La_{0.9}Sr_{0.1}Mn_{0.5}Ni_{0.5}O_3$ sample.

| Temperature [K] | | 4 | 300 |
|---|---|---|---|
| Space group | | R-3 | R-3 |
| a [Å] | | 5.4911(1) | 5.4950(1) |
| c [Å] | | 13.2014(2) | 13.2437(2) |
| V [Å³] | | 344.728(6) | 346.317(7) |
| La/Sr: | x | 0 | 0 |
| | y | 0 | 0 |
| | z | 0.2509(3) | 0.2519(4) |
| Biso [Å²] | | 0.12(4) | 0.55(4) |
| *Mn: | (x y z) | (0 0 ½) | (0 0 ½) |
| Biso [Å²] | | 0.43(7) | 0.53(7) |
| *Ni: | (x y z) | (0 0 0) | (0 0 0) |
| Biso [Å²] | | 0.43(7) | 0.53(7) |
| O: | x | 0.5501(5) | 0.5468(5) |
| | y | -0.0018(9) | -0.0049(8) |
| | z | 0.2506(3) | 0.2508(3) |
| Biso [Å²] | | 0.44(3) | 0.81(3) |
| $\mu_F$ [$\mu_B$] | | 0.9 | – |
| $\mu_{AF}$ [$\mu_B$] | | 0.4 | – |
| $\chi^2/R_{wp}$[%] | | 2.30/4.12 | 2.65/4.37 |
| $R_{Bragg}$[%]/$R_{mag}$[%] | | 2.68/47.4 | 5.47/ – |

The most reasonable argumentation of the obtained experimental data assumes that the compound contains the structural regions of well-ordered $Ni^{2+}$ and $Mn^{4+}$ ions. These regions are characterized by a maximal number of positive exchange interactions which governs high Curie point and magnetization. Other structural regions are considered to possess mainly $Ni^{3+}$ and $Mn^3$ ions which are disordered in the lattice and antiferromagnetic interactions become to be dominant thus decreasing the magnetization and a transition temperature. The chemical substitution by $Sr^{2+}$ ions transforms all manganese ions into the 4+ oxidation state while the structural order remains stable in spite of the presence of $Ni^{3+}$ ions and most probably negative interaction between $Ni^{3+}$ and $Mn^{4+}$ ions. In the case than the positive component of the superexchange interaction is nearly equal to the negative one it is possible than the critical temperatures of the transitions to the paramagnetic state of these magnetic phases is nearly coincide and the structural order remains to be stable.

**Conclusions**
The magnetization and transport properties of the compounds $LaMn_{0.5}Ni_{0.5}O_3$ with chemical substitution of $La^{3+}$ ions by $Sr^{2+}$ ones have been investigated using neutron diffraction method, magnetometry and magnetoresistance measurements. It is shown that chemical substitution by $Sr^{2+}$ ions leads to a modification of dominant magnetic state from ferromagnetic towards antiferromagnetic one even at low concentration of $Sr^{2+}$ content. The Curie temperature of the pristine compound is nearly coincide with that estimated for the doped compounds. Magnetoresistance effect decreases upon temperature increase and $Sr^{2+}$ content. The obtained results are discussed in the model which assumes that positive and negative components of the superexchange interaction $Ni^{2+}$-O-$Mn^{4+}$ are nearly equal to each other, the interaction between $Ni^{3+}$-O-$Mn^{4+}$ is negative. Large negative magnetoresistance effect is associated with structural and magnetic disorder as well as relatively large 3d-O2p hybridization which strengthens in magnetic field.

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